THE DECENNIAL PUBLICATIONS OF
THE UNIVERSITY OF CHICAGO

THE DECENNIAL PUBLICATIONS

ISSUED IN COMMEMORATION OF THE COMPLETION OF THE FIRST TEN YEARS OF THE UNIVERSITY'S EXISTENCE

AUTHORIZED BY THE BOARD OF TRUSTEES ON THE RECOMMENDATION OF THE PRESIDENT AND SENATE

EDITED BY A COMMITTEE APPOINTED BY THE SENATE

EDWARD CAPPS
STARR WILLARD CUTTING   ROLLIN D. SALISBURY
JAMES ROWLAND ANGELL   WILLIAM I. THOMAS   SHAILER MATHEWS
CARL DARLING BUCK   FREDERIC IVES CARPENTER   OSKAR BOLZA
JULIUS STIEGLITZ   JACQUES LOEB

THESE VOLUMES ARE DEDICATED

TO THE MEN AND WOMEN
OF OUR TIME AND COUNTRY WHO BY WISE AND GENEROUS GIVING
HAVE ENCOURAGED THE SEARCH AFTER TRUTH
IN ALL DEPARTMENTS OF KNOWLEDGE

PHYSICAL CHEMISTRY IN THE SERVICE OF THE SCIENCES

PHYSICAL CHEMISTRY IN THE SERVICE OF THE SCIENCES

MUI
CENT
COLL

BY

JACOBUS H. VAN 'T HOFF

MEMBER OF THE PRUSSIAN ACADEMY OF SCIENCES, PROFESSOR ORDINARIUS HONORARIUS IN
THE UNIVERSITY OF BERLIN, SPECIAL LECTURER AT THE DECENNIAL
CELEBRATION OF THE UNIVERSITY OF CHICAGO

ENGLISH VERSION BY

ALEXANDER SMITH

OF THE DEPARTMENT OF CHEMISTRY

THE DECENNIAL PUBLICATIONS
SECOND SERIES VOLUME XVIII

CHICAGO
THE UNIVERSITY OF CHICAGO PRESS
1903

Copyright 1903
BY THE UNIVERSITY OF CHICAGO

HERRN DR. WILLIAM RAINEY HARPER,
PRESIDENTEN DER UNIVERSITÄT CHICAGO,

der mit einem Organisations-Talent, das mich mit Bewunderung erfüllt, innerhalb zehn Jahre eine grosse Universität ins Leben gerufen hat, möchte ich diese englische Ausgabe meines Werkes widmen. Dass unter seiner Führerschaft der Einfluss, welchen sich die junge Anstalt schon zu verschaffen gewusst hat, von Jahr zu Jahr an Ausdehnung und Tiefe gewinnen möge, ist mein aufrichtiger Wunsch.

J. H. VAN 'T HOFF.

CHARLOTTENBURG,
16ten Juni, 1903.

AUTHOR'S PREFACE

The following lectures, delivered June 20–24, 1901, were given at the invitation of the University of Chicago on the occasion of the decennium of its foundation. The time for preparation being limited, the lectures were given extempore and the version here presented was adapted for publication from the stenographic report. In order that the whole may present as far as possible a memorial of the interesting festival, the changes made have been confined within the narrowest possible limits. The introductory lecture, which appears in this volume as the first lecture of the series, was delivered as one of the addresses before a general educational conference, held in the lecture theater of the Kent Chemical Laboratory, to which the guests of the University were invited.

Charlottenburg,
January, 1902.

PREFACE TO THE ENGLISH VERSION

During the festivities in connection with the celebration of the decennium of its foundation, the University of Chicago was honored by the presence of a number of the most distinguished scientific men of the world. Among these, Professor van 't Hoff, who received the honorary degree of LL.D., was one of the most prominent.

As this volume is in some degree a memorial of Professor van 't Hoff's visit, no apology need be offered for printing here the words pronounced by the President of the University when, at the convocation ceremony of Tuesday, June 18, 1901, the honorary degree was conferred:

JACOB HENRY VAN 'T HOFF,

> Professor of Physical Chemistry in the University of Berlin; investigator who has brought to bear upon chemical problems a keen and logical mind; endowed with speculative and imaginative powers of the highest order; founder of the theory explaining the space relations of atoms in molecules—a theory which is essential to a comprehension of the chemistry of organized and inorganized matter; master in the field of dynamic chemistry; investigator and brilliant discoverer in the domain of the modern theory of solutions—a theory which constitutes one of the greatest advances made by chemical science in the last quarter of a century: for these splendid and fertile achievements, by the

authority of the Board of Trustees of the University of Chicago, upon nomination of the University Senate, I confer upon you the degree of Doctor of Laws of this University, with all the rights and privileges appertaining thereunto.

Professor van 't Hoff most cordially consented, not only thus to visit the United States as one of the guests of the University, but also, at the special request of the Department of Chemistry, to deliver a course of lectures on that branch of chemistry which owes so large a share of its recent development to his brilliant and profound investigations.

The lectures were delivered in English, and, in slightly condensed form, are reproduced in this volume. The interest which they aroused was most gratifying both to the lecturer and to his hosts. They were attended by large audiences, which included professors of chemistry and related sciences from many distant states of the Union. Those who had the privilege of hearing them will not soon forget the genial personality of the speaker, the simple and lucid language, and the suggestive treatment which combined to make them memorable.

The excellent portrait, a reproduction of which forms the frontispiece, will give added interest to the book.

The plate showing a sheet of tin attacked by the "tin-disease" was made from a photograph kindly furnished by Dr. Ernst Cohen.

ALEXANDER SMITH.

CHICAGO, AUGUST, 1902.

TABLE OF CONTENTS

INTRODUCTORY

PAGE

LECTURE I - - - - - - - - - - - - 3

Kekulé's View, that Thirty Years Ago Chemistry Had Reached a Dead Point—Structural Chemistry Leads to Stereochemistry—The New Physical Chemistry—The Genius of Physical Chemistry Exhibited by Discussion of Osmotic Pressure—Calculation of Osmotic Pressure from Temperature and Concentration—Applications of the Conception of Osmotic Pressure in Biology—Loeb's Fertilization Experiment.

PHYSICAL CHEMISTRY AND PURE CHEMISTRY

LECTURE II - - - - - - - - - - - - 15

Plan of the Lectures—Modern Physical Chemistry Distinguished from the Earlier Physical Chemistry, and its Nature Defined—It Rests on Two Foundations: the Extension of Avogadro's Law to Solutions, and Thermodynamics—The Extension of Avogadro's Law—The Thermodynamical Principle of the Conservation of Energy—The Thermodynamical Principle of Carnot-Clausius—Reversible Cycles—Illustrations of the Application of These Principles—The First Great Service of Physical Chemistry in the Field of Pure Chemistry—Application of a New and Comprehensive Principle for the Study of Inorganic Problems—Case of Carnallite as Illustration—Graphic Representation of the Results.

LECTURE III - - - - - - - - - - - - 31

The Second Great Achievement of Physical Chemistry in the Field of Pure Chemistry—Berthelot's Principle of Maximum Work—Many Facts Contradict It—The New Conception that Change Occurs Only When Work Can Be Done—The

PAGE

Methods of Determining Which Changes Will Be Able to Do Work—The Thermochemical Method—The Electrical Method—The Third Great Achievement of Physical Chemistry in the Field of Pure Chemistry—The Theory of Ionization—Qualitative and Quantitative Illustrations of the Use of This Theory.

PHYSICAL CHEMISTRY AND INDUSTRIAL CHEMISTRY

LECTURE IV - - - - - - - - - - - - - 45

The Co-operation of Physical and Industrial Chemistry—Two Illustrations to Be Discussed—Results of Scientific Study of Carnallite and Possibilities of Their Commercial Application to the Manufacture of Potassium Chloride—The Recent Discoveries in Connection with Alloys and Steel, Introduced by a Description of the Peculiar Behavior of Tin, and its Explanation—White and Gray Tin and Their Transition Point at 20°—The Methods of Determining the Transition Point—Use of the Dilatometer—The Electrical Method.

LECTURE V - - - - - - - - - - - - - 58

Results of the Physico-Chemical Study of Wrought Iron, Cast Iron, and Steel—Complications Introduced by the Presence of Carbon and the Occurrence of Solid Solutions—Method of Studying Iron by Polishing, Etching, and the Use of the Microscope—Constituents are Ferrite, or Pure Iron; Martensite, or the Solid Solution of Carbon in Iron; Cementite, or the Carbide of Iron; Graphite, or Free Carbon; Pearlite, or the Cryohydratic Mass—Two Forms of Ferrite with Transition Point at 850°—Pearlite, a Mixture of Cementite and Ferrite, and its Formation and Composition—Hard Steel is Overcooled Martensite—The Graphite—The Behavior of Melted Iron Rich in Carbon—Rapid Cooling Gives White Cast Iron Containing Much Cementite—Slow Cooling Gives Gray Cast Iron by Decomposition of the Cementite and Production of Graphite, and Finally Pearlite—A Numerical Illustration of the Behavior of Molten Iron Containing 6⅔ per Cent. of Carbon When Cooled (1) Rapidly and (2) Slowly.

PHYSICAL CHEMISTRY AND PHYSIOLOGY

PAGE
LECTURE VI - - - - - - - - - - - - - 73

The Theory of Solutions Based upon the Extension of Avogadro's Principle and its Importance in Physiology—Osmotic Pressure and Osmotic Phenomena—The Experiments of de Vries with Plant Cells—The Work of Donders and Hamburger with Blood Corpuscles—The Experiment of Massart with the Human Eye and with Bacteria—Loeb's Work on Artificial Fertilization—The Measurement of Osmotic Pressure—Observation of the Freezing Points for Determining Equality of Osmotic Pressure—Specific Action of Ions in Physiology.

LECTURE VII - - - - - - - - - - - - 84

Enzymes, Their Preparation and Nature—Enzymes as Catalytic Agents—Chemical Equilibrium—Graphic Representation of Incomplete Chemical Interactions—Incomplete Actions Occur When the Heat Change is Small—Application to the Behavior of Enzymes—Illustrations—The Synthesis of Amygdalin.

PHYSICAL CHEMISTRY AND GEOLOGY

LECTURE VIII - - - - - - - - - - - 97

The Formation and Structure of Geological Salt Deposits—Early Study of Deposition from Solutions Containing Several Salts, by Usiglio—The Proportion of the Constituents as Well as Their Solubility to Be Considered—The Modern Method of Study and Graphic Representation—The Case of a Single Salt and Water at a Fixed Temperature, 25°—The Case of Two Salts Simultaneously Present at 25°—The Case of Three Salts at 25°—The Problem of Sea-Water at 25°, with All Salts Present.

PAGE

LECTURE IX - - - - - - - - - - - 115

The Influence of Time and of Variations in Temperature and Pressure on Deposition—The Time Factor and Delayed Crystallization—Several Compounds, Found in Nature, Do Not Appear at All in Laboratory Experiments on Deposition, But Can Be Included in the Scheme by the New Method of Agitation with Solutions—The Behavior at Temperatures above 25°—New Minerals Formed above 25° and Absent at 25°—New Combinations of Minerals Possible above 25°—Disappearance above 25° of Minerals Formed at That Temperature—The Influence of Possible Changes in Pressure is Too Slight to Affect the Results

INDEX - - - - - - - - - - - 125

INTRODUCTORY

LECTURE I

INTRODUCTORY

Kekulé's View, that Thirty Years Ago Chemistry Had Reached a Dead Point—Structural Chemistry Leads to Stereochemistry—The New Physical Chemistry—The Genius of Physical Chemistry Exhibited by Discussion of Osmotic Pressure—Calculation of Osmotic Pressure from Temperature and Concentration—Applications of the Conception of Osmotic Pressure in Biology—Loeb's Fertilization Experiment.

INASMUCH as during the next few days I am to deliver a number of lectures on certain topics of a physico-chemical nature, I should like to throw my address before this educational conference into the form of an introduction to these lectures.

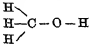
I must begin by saying at the outset that one of our best modern historians of the science of chemistry, Ladenburg,[1] expresses the opinion that the most characteristic feature of the chemistry of the last fifteen or twenty years is the continued increase in the prominence of this physical, or, as many say, general, chemistry. Will you allow me, therefore, briefly to explain how this physical chemistry has been developed, and what its present importance is, and will you permit me in doing so to refer to personal recollections to some extent?

Thirty years ago, when, as a young student in the University of Bonn, I first became acquainted with the science of chemistry, under the instruction of one of the most noted of chemists, Kekulé, that science was pronounced by our master to have reached a dead point, and to be without visible prospect of new advance.

---

[1] *Entwickelung der Chemie in den letzten 20 Jahren*, Stuttgart, 1900.

At that time the belief in the existence of atoms, although only an indirect conclusion from chemical facts, seemed to be well-founded. The molecular theory, which had been chiefly developed in connection with physics, lent strong support to it. The details in regard to the relations of the atoms in the molecule were known, or at all events the attainment of this knowledge in the case of the more complex or newer substances was only a question of time. Thus, the formula of methyl alcohol was:



This expressed the fact that in a molecule of this substance, four hydrogen atoms, each represented by the letter H, along with one atom of carbon and one of oxygen, represented respectively by the letters C and O, were present, and that they were attached to one another in the manner shown by the connecting lines.

Realistic as this conception was, it was very clearly recognized that such symbols were but mental pictures or diagrams on paper, and chemistry was looking for some Newton who should discover the laws according to which the atoms themselves were held together in their molecular configuration to form one complete whole.

As we probably are all aware, however, no Newton of this kind arrived, and yet only a few years after Kekulé's unfortunate utterance (a sort of remark, we may say in passing, such as a teacher ought perhaps never to make before his pupils) there arose the conceptions of stereochemistry, giving birth to a new, but now well-developed and vigorous, branch of our science.

By means of stereochemistry so much at least was accomplished that, the real existence of the atoms being assumed, not only was their mode of union described but also their relative positions in the molecule was determined. The above symbol for methyl alcohol now became a tridimensional model, with the carbon in the center of a tetrahedron, at whose four equidistant points the three hydrogen atoms and the hydroxyl group were situated.

We remained, however, and after twenty-five years still remain, unacquainted with the laws which control these relative positions. Perhaps, by the help of the new conception of electrons, we may be on the eve of getting a clearer knowledge of the condition of the atoms, at least in the neighborhood of the absolute zero of temperature.

During these twenty-five years, however, investigation still proceeded, although in an entirely different direction. It did not advance by the elaboration of symbol architecture, with atoms as the bricks. About fifteen years after Kekulé's unfortunate expression, a second child of hope, the new physical chemistry, came into being. It did not arise all at once: there is hardly a branch of science in which this occurs. It was developed like a small plant, unseen in the shade; at length it feels the sun and promises to expand into a colossal tree.

Some, like Duhem,[1] go so far as to claim for physical chemistry the rank of a third science, and range it beside the sciences of physics and chemistry. Others, like Winkler[2] and Ladenburg, favor the view that a prominent place *within* the territory of chemistry should be devoted to physical chemistry, and that the previous subdivision into organic and inorganic should be replaced by a division into three. In this connection, it is of interest to mention that at the present moment the University of Göttingen is planning to organize its chemical department on this basis.

Leaving aside all principles of subdivision, which must always be of an arbitrary nature, since science, like that nature which it reflects, must be one great whole, I should like here to answer the question, What has this physical chemistry brought to pass?

This question may be taken in either one of two ways, general and particular, and answered accordingly. One might, on the one hand, exhibit the general conclusions, and, taking this sense, I should have to speak of the laws of chemical change, of reaction speed, and of electrochemical processes. Yet even so I should be unable to do this without using complicated formulæ, which the character of this introduction forbids.

On the other hand, the genius of physical chemistry may be portrayed by a study of one of the special problems which it has been in a position to solve. It is in this direction that I prefer to proceed in answering the above question, and I shall ask your attention to one of the best known and most far-reaching achievements of physical chemistry. It is connected with the establishment and application of the conception of osmotic pressure.

---

[1] "Une science nouvelle. La chimie physique," *Revue philomatique de Bordeaux et du Sud-Ouest*, 1899.

[2] *Berichte d. deutsch. chem. Gesell.*, Vol XXXIV, p. 399.

By way of approaching this special problem, consider the attraction for water shown by some well-known substances, like quicklime. If a bottle is filled up with this and is loosely stoppered, the lime will attract water from the moist air, will swell up, and, finally, no matter how strong the bottle may be, will inevitably break the vessel which contains it. An enormous force is developed by this attraction for water, so great that it has not been found possible to subject the pressure to exact measurement.

A similar but less violent phenomenon can be observed, and may be measured, provided we confine ourselves to dilute solutions. Thus, sugar, even in dilute solution, shows this attraction for water to a marked degree. We take, following Pfeffer,[1] a one per cent. solution of sugar, and fill with it a vessel whose walls are porous, so as to permit the passage of the water alone. A suitably prepared battery jar will serve the purpose. We place this, after closing it, in pure water, and find that the latter, attracted by the sugar solution, forces its way through the porous wall until at 7°, if the vessel is sufficiently strong to withstand it, a pressure of two-thirds of an atmosphere is attained. This sort of pressure is called osmotic pressure.

We can now proceed further to generalize, and say that every substance capable of dissolving will attract the solvent. This is, in fact, only another way of referring to the tendency to dissolve. Conversely, the solid substance is in turn attracted by the solvent, and diffuses into it when it is furnished an opportunity to do so. In the latter case the osmotic pressure appears in another light, and becomes the pressure which prevents the undissolved molecules from freely moving into the surrounding solvent, when a state of saturation has been reached. After the same fashion, gas molecules exercise gaseous pressure in the direction of an empty space when they are hindered by a partition from entering it.

---

[1] *Osmotische Untersuchungen*, Leipzig, 1877.

This osmotic pressure was studied as early as a hundred years ago, especially with reference to its significance in physiological processes. It was found to have a definite value. This seemed, at first, to be dependent upon the nature of the membrane, to vary with the nature of the dissolved substance and of the solvent, to be obviously dependent upon the concentration, and likewise to be very sensitive to change of temperature. These were essentially the facts known about osmotic pressure up to the time at which the path being blazed by physical chemistry encountered it.

The result was unexpectedly simple. So plain was it that now one can even calculate the osmotic pressure (for a dilute solution of a non-electrolyte) when the concentration and temperature are given. The whole relation is, in fact, presented in the expression

$$P = 0.08\,CT\ ,$$

in which P is the osmotic pressure in atmospheres, T the absolute temperature, and C the concentration or the number of gram-molecules of the dissolved body per liter of solution. The numerical value of Pfeffer's observation upon the one per cent. solution of sugar, in which $T = 273° + 7°$ or $280°$ and $C = \frac{10}{342}$, is obtained at once from the above formula.

I should like to emphasize the differences in the methods of physical chemistry and its manner of procedure when compared with those of stereochemistry. The former does not primarily seek the solution of its problems in any conception of the nature of matter. The above formula contains, so far as this is concerned, only the relative molecular weight, which, where investigation in the form of a gas is possible, corresponds to the gas density. Physical chemistry therefore confines itself to numerical relations between directly measurable magnitudes.

In spite of the limitation which physical chemistry thus imposes upon itself, it is certainly a strong evidence of its sound foundation and healthy power to develop that it shows itself, in a continually increasing degree, capable of solving those problems which, on account of their direct relation to life, seem to be the most complex. If we take into consideration the colossal labors which were spent in the service of atomic conceptions, it must be admitted that relatively little has been accomplished by them in this particular direction. The very opposite can be stated of the labors of the physical chemist. As long as ten years ago, in Utrecht,[1]

---

[1] "Over de physiologische beteekenis der jongste stroomingen op chemisch physisch gebied," *Natuur- en Geneeskundig Congres*, Utrecht, 1891.

I employed an opportunity like the present to refer to the tremendous rôle which osmotic pressure, whose laws have been laid bare by physical chemistry, plays in many of the processes of living organisms.

At that time I was able to present the results of several physiological investigations, which tended to show that osmotic pressure is a fundamental factor in the most various life-functions of animals and plants. According to de Vries[1] it regulates the growth of plants. According to Donders and Hamburger[2] it regulates the functions of the red blood corpuscles, and thus of the blood. According to Massart[3] it controls some of the functions of the human eye, as well as the life of the seeds of disease, and deadly organisms like the bacilli of typhoid fever.

Since that time the literature of this subject has grown until it would easily fill a large and comprehensive volume.[4] Perhaps the most pregnant fact of all is that which has been established in this very University of Chicago by Loeb. It is to the effect that the act of fertilization of lower animals, like sea-urchins, can be in part replaced by a definite increase in the osmotic pressure of the liquid in which the unfertilized egg is lying. The development starts and even proceeds to the production of a motile organism. I may most fitly conclude in the words with which the investigator just named closed an address[1] given on the present subject: "At no time since the period immediately following the discovery of the law of conservation of energy has the outlook for the progress of physiology appeared brighter than at present, this largely being due to the application of physical chemistry to the problems of life."

---

[1] "Eine Methode zur Analyse der Turgorkraft," *Pringsheims Jahrbücher*, Vol. XIV.

[2] *Onderzoekingen gedaan in het physiologisch Laboratorium der Utrechtsche Hoogeschool*, (3), Vol IX, p 26.

[3] *Extrait des archives de biologie*, Liège, 1889

[4] A compilation extending to 1900 is given by Koeppe, *Physikalische Chemie in der Medizin*, Wien, 1900. See also the very full bibliography in Burton E. Livingston's *Rôle of Diffusion and Osmotic Pressure in Plants*, University of Chicago Press, 1903.

---

[1] "The Physiological Problems of Today," *American Society of Naturalists*, Ithaca, 1897.

PHYSICAL CHEMISTRY AND PURE CHEMISTRY

LECTURE II

PHYSICAL CHEMISTRY AND PURE CHEMISTRY

Plan of the Lectures—Modern Physical Chemistry Distinguished from the Earlier Physical Chemistry, and its Nature Defined—It Rests on Two Foundations, the Extension of Avogadro's Law to Solutions and Thermodynamics—The Extension of Avogadro's Law—The Thermodynamical Principle of the Conservation of Energy—The Thermodynamical Principle of Carnot-Clausius—Reversible Cycles—Illustrations of the Application of These Principles—The First Great Service of Physical Chemistry in the Field of Pure Chemistry—Application of a New and Comprehensive Principle for the Study of Inorganic Problems—Case of Carnallite as Illustration—Graphic Representation of the Results.

I WILL begin by setting before you the scheme of that which I desire to develop in these lectures. I have divided the material into four parts, each of which refers to physical chemistry, but gives a view from a different standpoint. The object of this is to show the relations to, and the influence upon, different branches of science, pure or applied, which physical chemistry is able to exhibit.

I should wish to consider physical chemistry, in the first place, in its application to pure chemistry, and, in the second place, in its relation to applied or technical chemistry. Then I shall devote two lectures to the relation of physical chemistry to physiology, since the characteristic of the development of physiology in recent years seems to lie in the fact that it has made application of physico-chemical methods.

Finally, I should like to show by a few examples how physical chemistry attempts to attack geological problems.

Beginning with the relation between physical chemistry and pure chemistry, I must first briefly delimit that which at the present day we understand by the former title. If we take the expression in its most general sense, it refers evidently to the application of physical expedients, methods, and instruments to chemical problems. Interpreted in this way, one might state that when Lavoisier made chemistry the science which it is, he simultaneously founded physical chemistry. He did this inasmuch as he applied the balance, obviously a physical instrument, to the testing and establishing of fundamental laws in the realm of chemistry. Later, when Bunsen, in his universally-known investigations with the spectroscope, determined the composition of the sun and stars, it could be said with equal right that physical chemistry was involved, since the spectroscope is classed as a piece of physical apparatus. In this way ever greater advances in our science have been bound up with the introduction of physical methods of observation and measurement.

Apart from this, it is said, and said correctly, that physical chemistry is a recent development of the last fifteen years.[1] I should like to explain in what way this last phase in its development may be considered as having especially profound significance. The introduction of the spectroscope by Bunsen, and the later employment of the calorimeter in the chemical laboratory by Berthelot and Thomson, were of the highest importance, but were limited to a particular manifestation, such as the emission of light or the production of heat. Now, what physical chemistry in the latest period has done, or has claimed to do, did not consist in the introduction of new apparatus or of a new method of observation. The most recent development of physical chemistry has been characterized rather by the establishment of comprehensive principles which fertilize the whole foundation of the science, and promise to furnish nourishment for a large part of the chemistry of the future. I should be glad if I could exhibit one of these fundamental principles in application before you in the same manner as a lecture-experiment is shown. Yet this practical procedure is precisely that which the character of the new development expressly excludes, since it has not brought into use essentially new apparatus and methods, but rather new laws, which are unfortunately not of the simplest description.

---

[1] NERNST, *Address at the Opening of the Institute of Physical Chemistry and Electro-chemistry*, Göttingen, 1896.

I remember very well that as a student I was never able to understand the real import of Avogadro's law, and that I received the first glimpse of its bearing when I explained it in teaching and applied it in experiment. And yet the principles which I have to lay before you are still further removed by their abstract character from the range of everyday thought than even the law of Avogadro. If, therefore, I were to attempt to build up these principles from their foundations, those to whom they were new would probably find their time had been wasted, since they would have no opportunity for gaining a correct understanding of them by actual application. On the other hand, those to whom these principles are already known might justly complain that nothing new had been set before them.

Thus I have considered it most advisable not to enter upon the study of these principles very deeply, but to assume them as known. I shall prefer to take for detailed consideration the application of these principles to the answering of definite questions, and thus, so far as possible, to break new ground.

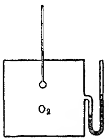


FIG. 1

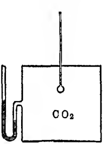


FIG. 2

There are in the main two foundations on which the recent development of physical chemistry rests: the extension of the law of Avogadro and thermodynamics. The particular extension of Avogadro's law referred to may easily be connected with the content of the original rule when the latter is expressed in the following form: If we take a fixed volume (Fig. 1) of any gas, for example, oxygen, then we know that it exercises a pressure upon the walls of the vessel. This pressure, probably produced by the impact of the molecules, may be measured by a manometer such as that shown in the figure. Its value depends upon the temperature and we may assume this to be recorded by the thermometer and to be, for example, 20°. Now, Avogadro's rule states that if into an equal space (Fig. 2) we introduce so much of another gas, for example carbon dioxide, that at the same temperature (20°) an equal pressure is exercised, then both spaces must contain equal numbers of molecules of their respective gases. We might consider this number to be 1000 in each case. The absolute number is unknown and only the equality in the number is postulated.

The expansion of this principle is concerned with solutions. In these also an effect comparable with gaseous pressure is exercised. The gaseous pressure has to do with the fact that a gas endeavors to diffuse into a vacant space and thus presses upon the impermeable walls, which prevent its further progress. In the same way, in a solution, also, the dissolved substances tend to diffuse into the pure solvent when the solution and solvent are in contact. This may be seen when the liquids are carefully placed one above the other in the same vessel in such a way that that which is specifically lighter is placed upon the top. A partition, impermeable by the dissolved body, which did not interfere with contact between the solution and the solvent (which, in other words, was permeable by the solvent), would restrain this diffusion and experience a pressure. This pressure is obviously the so-called osmotic pressure which has already been mentioned (p. 7) in the introduction. The extension of Avogadro's principle consists in this: that for a given substance the osmotic pressure is equal in value to the gaseous pressure, provided the temperatures and the concentrations, that is, the quantities in unit volume, are the same. From this it follows immediately that two solutions of different bodies containing equal numbers of molecules in equal volumes, provided they are at the same temperature, exercise the same osmotic pressure. Not only so, but when the molecular weight is known, this pressure, like the gaseous pressure, can be calculated with ease. For our purpose, it is unnecessary to pursue this law by further numerical illustration. We shall add only that this law of Avogadro and its extension (and be it remarked, the extension is a most comprehensive one, since it applies to all soluble bodies and to all solvents) is restricted in its application within certain limits. It claims strict accuracy, both in the original and extended forms, only when the dilution is very great, or, in other words, only under conditions which cannot be realized practically. Nevertheless, at dilutions which correspond to that of atmospheric air, that is to say, in the case of gases at a pressure of one atmosphere and in the case of solutions of an analogous concentration (about one-tenth normal), the deviations, in most cases where the principles find application, are insignificant.

So much for the first principle which has contributed to the recent development of physical chemistry, and is often named the theory of solutions. The second concerns the application of thermodynamics, and particularly of the law of conservation of work or energy, and of the Carnot-Clausius principle to chemical questions. What I said in the beginning about Avogadro's law, to the effect that the correct appreciation of its content can be reached by most students only after application to definite problems encountered in independent research, might be said perhaps with even greater truth of the principle which is now to be discussed.

The principle of the conservation of energy is in itself simple enough. No energy arises or disappears. Change in form in an unchanging amount is alone possible. The forms with which we have to do in the treatment of chemical problems are in the main mechanical work, heat, light, and electrical energy. The whole preliminary knowledge required consists in knowing that when mechanical work is converted into heat 425 kilogram-meters give exactly one calorie; when electric energy is turned into heat, one gram-equivalent at a tension of one volt gives 23 calories.

The Carnot-Clausius principle is far from simple. This conception, again, I never understood until I had occasion to apply it in my investigations, and to test it in numerical calculations. While Avogadro's law can be stated in few words, this is impossible in the present case. Further, the principle of Carnot-Clausius finds expression in so many different forms that even after practice it is not very easy to handle. Since it is possible that among the younger students of science present there may still be some who have yet to take their first step into this region by applying its conceptions to chemical problems, I shall make a suggestion as to the choice of the most suitable form of this principle. It may be applied by carrying out so-called reversible cycles of operations or by the introduction of abstract physical conceptions and mathematical functions, such as entropy, as is done by physicists like Gibbs, Planck, and Duhem. I am convinced that, for the chemist, the first form, in which reversible cycles are employed, is the most advantageous. The difficulty that is then encountered is confined to the conception of a "reversible cycle."

Briefly stated, a cycle consists in a series of changes in course of which the original condition is reached. Thus, for example, we permit ice to evaporate, condense the vapor to water, and then freeze the water. These changes are reversible, provided they take place under such conditions that the change can proceed in either direction. This is true, for example, when water is frozen in a region where the temperature is 0° C., and where, therefore, ice can just as well melt. At temperatures above or below 0° only one or other of these processes can take place. Now, in such a cycle of operations—and this is the content of the Carnot-Clausius principle—the sum of the quantities of heat (Q), divided by the absolute temperature (T) at which it is communicated, is equal to zero.

$$\sum \frac{Q}{T} = 0 \ .$$

A very simple application which frequently throws an unexpected light on chemical problems is to be noted when the reversible cycle is carried out at constant temperature. Here the equation obviously becomes:

$$\Sigma Q = 0 \ .$$

That is to say, the sum of the heats communicated is equal to zero, or, in other words, no heat passes into any other form of energy, such as, for example, mechanical work. The sum of the work (A) accomplished in the course of the operations is, therefore, likewise zero.

$$\Sigma A = 0 \ .$$

Applying this, for instance, to the above cycle with ice-water and vapor, we draw at once the important conclusion that at 0° the vapor tension of water and ice must be equal. Considering processes more closely allied to chemistry—such as the reversible change of rhombic and monoclinic sulphur at 96°, and that of cyamelid and cyanuric acid at 150°—we infer that there must be equality in each case between the vapor tensions of the two forms of sulphur, and between the so-called dissociation pressures of cyamelid and cyanuric acid at the point of change into gaseous cyanic acid. In the latter case we encounter another great advantage in the application of the Carnot-Clausius principle. This is that the complexity of the nature of the process under consideration does not introduce the slightest difficulty. The composition of the bodies, for example, is of so little importance that atomic and molecular conceptions need not be considered, and, strictly speaking, in the last-mentioned case, it need only be known that cyanuric acid, cyamelid, and cyanic acid have the same percentage composition, since otherwise the cycle of operations could not be carried out.

I must limit myself to the foregoing brief remarks on the principles of Avogadro and Carnot-Clausius, and proceed to lay before you what is attainable by their application. In doing this I must first refer to those who, few in number and not always working under the most favorable conditions, during the last fifteen years have brought physical chemistry to its present state of development. The very first place must be given to Ostwald, who by his comprehensive activity as a teacher, his astonishing literary labors, and his powers of organization has perhaps done more than any other for the spread of physical chemistry. I name along with him Arrhenius, whose introduction of the theory of electrolytic dissociation, and Nernst, whose application of the same theory, have opened up an entirely unsuspected field in the region of electric phenomena.

The greatest progress is promised and the greatest progress has been achieved by the application of physical chemistry to that part of the science which is usually designated inorganic. This includes all the elements save carbon, whose chemistry, as you know, is classed as organic. That new principles ultimately to be applied to the whole science are more easily introduced in connection with the former, depends on the simpler character of inorganic problems. Inorganic elements, like potassium and chlorine, give usually a single compound, like potassium chloride. When the element carbon (C) is taken into consideration, however, this is all changed, and the combination of this element with hydrogen (H), for example, offers a seemingly innumerable number of possibilities, such as CH_4, C_2H_4, C_2H_2, etc.

Glancing at what has been achieved in inorganic chemistry, three advances may be noted. First, it may be said that physical chemistry, in the handling of inorganic problems, has introduced an entirely new and comprehensive method of work. Secondly, we are in possession of a principle which enables us to foretell in what direction and how far a chemical change will proceed. Thirdly, physical chemistry has thrown new light on the nature of the solutions of the so-called electrolytes; that is to say, of bases, acids, and salts.

I hope to have the opportunity of illustrating each of these three achievements by describing a particular case. In order first to bring before you the new mode of treating inorganic problems, I shall describe its application to the study of carnallite, a mineral of technical importance, and known to be a compound (double salt) of magnesium chloride, potassium chloride, and water. Let me add that the investigation in question was carried out in co-operation with Meyerhoffer, but that the method of treating inorganic compounds which is illustrated by it was originally developed more particularly by Bakhuis-Roozeboom.

If you look up the subject of carnallite in the earlier text-books you will find the formula $MgCl_2 . KCl . 6H_2O$, with the statement that the compound is colorless and crystalline, and that it dissolves in water easily, with separation of potassium chloride. You will find also the method of preparation, and some further single, disconnected data. The new method of studying the subject leads, however, to a completely exhaustive knowledge of the subject. It is based essentially on a better comprehension of the equilibrium relationships in complex chemical phenomena, and of the influences which temperature, proportions of material, and pressure exercise upon them. We have, for example, discovered so-called transition temperatures in complicated chemical changes, which have the closest resemblance to simple physical melting-points. Thus, according as one passes above or below this temperature, a complete change in one direction or the other takes place. This change is, however, of a complex chemical nature. We have discovered the phase-rule in terms of which the most different sorts of equilibria can be uniformly interpreted. Finally, we have made easier, and in some cases for the first time made possible, the achievement of a knowledge of the whole circumstances of a chemical change in relation to temperature and pressure, by an extensive application of graphic methods. Carnallite presents an especially good example of the last, and I should like particularly to call your attention to the fact that a very minimum of observations puts us in possession of a complete knowledge of its whole behavior.

The problem before us is this: Carnallite being a compound of magnesium and potassium chlorides and water, what arises when these three substances are brought together in different proportions, at different temperatures, and the escape of the water is prevented? It is needless to add that all these conditions are easily realized in experimental work.

In considering this question we shall start from the beautiful transformation which carnallite undergoes in presence of water when the temperature is lowered.

If the amount of water added is not too great, a part of the carnallite is dissolved, some potassium chloride separates in solid form, and a corresponding excess of magnesium chloride is found in the solution. When the temperature is now lowered the dissolved quantities vary on account of changes in solubility. About −21°, however, a partial solidification of the liquid, akin to freezing, begins. This change resembles freezing also, in the fact that, in spite of continuous removal of heat, a thermometer shows that the temperature remains constant at −21°. The same constancy is observed when heat is added, while melting of a greater or less proportion of the solid part takes place. Approaching the study of the phenomenon more closely, we find that the carnallite at this temperature decomposes as heat is removed, and that water is taken up, according to the equation:

$$MgCl_2 . KCl . 6H_2O + 6H_2O = MgCl_2 . 12H_2O + KCl\ .$$

At −21° equilibrium exists between these two conditions, just as at 0° the same relation subsists between water and ice. On each side of this temperature one or other is alone stable. This relationship may be expressed by writing the equation in the form:

$$MgCl_2 . KCl . 6H_2O + 6H_2O \underset{-21^\circ}{\rightleftarrows} MgCl_2 . 12H_2O + KCl\ .$$

This statement, however, does not include all the facts in regard to the phenomenon, since the water in contact with the carnallite and the two other bodies has dissolved some of each substance, and the composition of this solution is expressed by the formula:

$$[H_2O + 0.066MgCl_2 + 0.005KCl].$$

Thus the exact equation has the following form:

$$0.208(MgCl_2 . KCl . 6H_2O) + 6[H_2O + 0.066MgCl_2 + 0.005KCl]$$
$$= 0.604(MgCl_2 . 12H_2O) + 0\ 238KCl\ .$$

When these proportions are employed, below −21° complete solidification takes place, while above it only potassium chloride and solution remain.

Viewing the system in relation to this chemical change, it must now be remarked that the solution which is there present, and whose composition has just been given, is the starting point of three series of saturated solutions which are obtained by changing the proportions of the materials. If, in the first place, we take somewhat more water, then even when the temperature is lowered the solution remains. It is saturated with $MgCl_2 . 12H_2O$ and potassium chloride, and has a definite composition peculiar to each temperature. We shall note this composition only at the point where a new transformation occurs. This is at $-34°$, where ice is formed. Here everything becomes solid, and the liquid disappears. At this point the composition of the solution is

$$[H_2O + 0.043MgCl_2 + 0.003KCl] .$$

If we now follow the relations at higher temperatures, two limiting cases are possible, according as an excess of $MgCl . 12H_2O$ or of KCl is present along with the carnallite. In the former case we encounter at $-17°$ the melting point of $MgCl_2 . 12H_2O$; in the latter at 168° that of the carnallite.

Time does not permit us to pursue the consideration of the subject in further detail, but it is obvious from what has been said that the conditions for the formation and existence of carnallite can be gradually delimited. In temperature they must lie between $-21°$ and 168°, and between these points the solutions from which carnallite is formed may have a maximum content either of magnesium chloride or potassium chloride up to saturation with either. Thus we find a region in which its existence is possible, and this region is capable of graphic representation.

Three axes are obviously required: one for the temperature, OX (Fig. 3), and two others for the amounts of $MgCl_2$ and KCl in the saturated solution, which are designated OY and OZ respectively. It is the composition of this solution that determines the nature of the solid bodies which will come out. Our transition temperature and the corresponding composition of the solution are represented by the point E. The three solubility curves proceeding from this point are ED, terminating in the freezing-point of the solution at

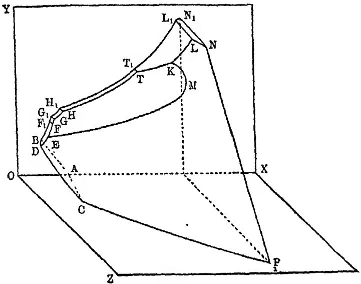


FIG. 3

D; EF, with the melting-point of $MgCl_2 . 12H_2O$ at F; EM, with the melting-point of carnallite at M. The whole carnallite area is bounded by EFGHTKM. Within this lie all the possible methods of forming it by employment of the simple components; on passing outside this area we encounter all the possibilities of partial or complete decomposition.

The rest of Fig. 3 has been obtained by the addition of data of a simpler kind which fit into the scheme as follows: In the plane XOZ lies the solubility curve of potassium chloride, CP, which marks the limit of the deposition of potassium chloride from pure water. Since the line DEM corresponds to the presence of the maximum amount of magnesium chloride, a potassium chloride area arises which is limited on the left by the boundary PCDEM. Similarly, a magnesium chloride area fits into this, complicated by the occurrence of various hydrates, which is bounded on the left by the line BF_1FED. An ice area closes the whole on the left and connects the three cryohydric points, B, C, and D, with A, which represents the freezing-point of pure water.

LECTURE III

PHYSICAL CHEMISTRY AND PURE CHEMISTRY

The Second Great Achievement of Physical Chemistry in the Field of Pure Chemistry—Berthelot's Principle of Maximum Work—Many Facts Contradict It—The New Conception that Change Occurs Only When Work Can Be Done—The Methods of Determining Which Changes Will Be Able to Do Work—The Thermochemical Method—The Electrical Method—The Third Great Achievement of Physical Chemistry in the Field of Pure Chemistry—The Theory of Ionization—Qualitative and Quantitative Illustrations of the Use of This Theory.

THE second service of physical chemistry to pure chemistry depends on the fact that it has established the fundamental principle which enables us to predict from other data whether a given chemical change will take place or not. When this chemical change is one which reaches a condition of equilibrium, as is often the case, then the principle permits also the prediction of the extent to which the change will go.

You may be aware that a principle of this kind was stated by Thomson and by Berthelot, and received from the latter the name of *principe du travail maximum.* This principle was a very simple one, since it stated merely that the heat which is developed by a chemical change indicates the direction in which the change will proceed: when the possibility of evolution of heat exists, then the reaction will proceed in such a direction as to bring this about. Take, for instance, hydrogen and oxygen. Two grams of the former with sixteen grams of the latter can develop 69 calories when uniting to form water. The principle just referred to sees in this possibility of heat development the cause of the formation of the water, which, as we know, takes place when the mixture of the gases is ignited. Conversely, if we consider nitrogen and chlorine, we find that by their union no heat will be developed; on the contrary, heat will be absorbed. So here, instead of a union of the elements, the tendency is toward the decomposition of the compound. When the union has been achieved by indirect means, decomposition can be brought about by the slightest shock. For many years this conception was a fundamental principle of thermochemistry, and numberless facts were known to support it.

In spite of this it is not difficult to furnish examples of cases in which chemical changes take place with absorption of heat. Freezing mixtures, like that of hydrochloric acid and Glauber's salt, whose operation depends on the accomplishment of a chemical change, in this particular case

$$Na_2SO_4 . 10H_2O + 2HCl \rightarrow 2NaCl + 10H_2O + H_2SO_4,$$

indicate the location of facts which contradict this "principle of maximum work." The greater number of reactions which proceed only to a certain limit, like the decomposition of calcium carbonate which ceases when a certain pressure of carbon dioxide has been obtained, likewise involve disproofs of the suggested principle.

Nevertheless, the expression "maximum work" was fortunately chosen, since the correct principle for the prediction of reactions must connect the possibility of a change with the possibility of a concomitant accomplishment of work. The newer conception is not less simple than the older, and is in a measure self-evident. Whenever any change whatever in the realm of nature can accomplish work, that is, can overcome resistance, it must proceed when the resistance is absent. This is true in particular of chemical changes. Now, it must be noted that the accomplishment of work and the development of heat in chemical changes do not mean quite the same thing. Often they do go hand in hand, as in the case of explosives like gunpowder and dynamite. These materials are familiarly known to furnish by their explosion great chemical means of doing work and at the same time to develop large quantities of heat. A compound like phosphonium chloride (PH_4Cl), however, a solid body, tends to decompose at ordinary temperatures into the gases phosphine (PH_3) and hydrogen chloride (HCl) with marked absorption of heat. Yet the decomposition products of this action may exercise a pressure of some twenty atmospheres. Here we have a case where the possibility of accomplishing work does not coincide with the capacity to develop heat, and yet where it is obviously the capacity to do work which controls the direction of the change.

The great difficulty in applying this new principle to the prediction of reactions lies, however, in finding a method for determining from other data the existence of the possibility of accomplishing work and the amount of this work in any given action. We know that Berthelot devoted half of his life to the systematic measurement of heats of reaction. Trusting in his principle he desired to present chemists with the data which appeared from this point of view to be suitable for the prediction of chemical changes. Since a change in the fundamental conception itself, however, has been shown to be necessary, another magnificent lifework has been suggested. This piece of research would require the repetition of all the investigations, carried out by Berthelot with the calorimeter, with the object of determining the ability of each reaction to do work. This task would be, however, incomparably more difficult than Berthelot's, since the possibility of accomplishing work depends in a much greater degree on the conditions, the temperature, and, in the case of dissolved bodies, the concentration, than does the heat development. This fact is in harmony with the great influence which these factors exert upon chemical changes.

Let us begin with a very simple example and consider the formation of carnallite at -21° according to the simplified equation:

$$MgCl_2 . 12H_2O + KCl = MgCl_2 . KCl . 6H_2O + 6H_2O.$$

Obviously, at -21° the possibility of doing work (E) of which the formation of carnallite is capable, is zero.

$$E = 0$$

Above -21° the reaction proceeds, however. It can, therefore, overcome a resistance, and since the reaction is accompanied by increase in volume this resistance might be a pressure. The maximum work will obviously be obtained in this case if the resistance is so great that the formation of carnallite is just able to take place and no more, while any increase in the pressure would cause a reversal of the change. Under these circumstances the transformation is reversible, and thus the principle of reversible cycles can be applied to it. The use of this principle leads to the expression

$$dE = -W\frac{dT}{T}$$

or for finite values

$$E = -W\frac{\Delta t}{T}\ .$$

This means that at a temperature dT (or Δt) degrees above the transition point, which in the present case is situated at 252° on the absolute scale, an amount of work dE (or E) can be accomplished. In applying this formula, since W is the heat of formation of carnallite by the action represented in the preceding equation, dE and W must be expressed in the same units, for example calories.

From the above expression the most essential fact may be read at once. At the transition temperature ($\Delta t = 0$) E has the value zero. Above and below this the sign of E changes. Here the sensitiveness to changes in temperature of the power to do work is most pronounced, and the sensitiveness of the direction of the chemical change to the same influence is most noticeable.

The principle of Berthelot now appears in a new light. If $\Delta t = -T$, that is to say, if the absolute zero is the temperature of experiment, then

$$E = W\ .$$

That is to say, under these circumstances, the heat developed will be a measure of the capacity to do work. The fact that Berthelot's principle under ordinary conditions so frequently gives satisfactory results depends chiefly on the fact that our ordinary temperature of experiment is relatively low, being only 273 degrees removed from the absolute zero. In the neighborhood of such a temperature as 1000° the whole circumstances are essentially different and usually the results are in conflict with Berthelot's law. Thus at that temperature acetylene is formed with absorption of heat, and water decomposes in spite of tho fact that its formation is accompanied by the evolution of heat.

We must also point out a second basis for the measurement of capacity for doing work which has been extremely fruitful. The relation of this capacity to do work to the possible accomplishment of mechanical work has already been referred to. Then we noted its relation to heat development. There remains still for consideration its relation to the production of electricity. Take a chemical change which develops electricity, like the displacement of copper by zinc in the Daniell cell,

$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu \ .$$

This reaction can just as well be overcome by a suitable resistance and forced to proceed in the reverse direction, as an action accompanied by increase in volume can be reversed by pressure Here, however, the opposing force must be of an electrical nature. As a matter of fact, when a current of electricity is applied in the reverse direction to a Daniell cell the amount of chemical change is at once diminished. The change can be brought to rest completely if the electromotive force of the contrary current is equal to that of the cell; and if it is greater the direction of the action may even be reversed. The electromotive force when electricity is produced corresponds therefore to the pressure when the chemical change tends to bring about an increase in volume. Detailed consideration from this point of view leads us to discover in the electromotive force a measure of the capacity to do work.

In all this we have a very rich field for working out the problem of predicting reactions, and this method brings within our grasp the prediction of reactions which are much less simple than those which, like the formation of carnallite, are characterized by a transition temperature, and whose whole behavior is defined when a single temperature is given. In this way, too, the more delicate, gradual displacement of a condition of chemical equilibrium under the influence of temperature and concentration is brought under control—a fact which has recently been demonstrated in a most striking manner.[1]

A chemical change which illustrates this, is the action of thallium chloride on potassium sulphocyanate solution. This takes place with so-called double decomposition according to the equation:

$$\mathrm{TlCl + KSCN = TlSCN + KCl} \;.$$

This change belongs, however, to those which reach a condition of rest before they have been completely accomplished, and lead to a so-called chemical equilibrium. This we represent in symbols thus:

---

[1] BREDIG UND KNÜPFFER, *Zeit. f. physik. Chem.*, Vol. XXVI, p. 260.

$$TlCl + KSCN \leftrightarrows TlSCN + KCl\ .$$

The condition of equilibrium exists not only at a definite temperature, as in the case of equilibria having transition points, but, as the temperature changes, is displaced gradually in one direction or the other with a corresponding alteration in the concentrations of the dissolved chloride and sulphocyanate of potassium.

The above change was employed for the construction of a galvanic cell, whose electromotive force was measured. The changes in this electromotive force brought about by alterations in temperature and concentration were studied. From this investigation the conditions were discovered under which the electromotive force became zero. In view of the small solubility of the thallium salts, this depended essentially on the concentration of the chloride and sulphocyanate of potassium. In a simultaneous study of the conditions when chemical equilibrium was reached, it was discovered that they corresponded exactly to those at which the electromotive force became zero. We were thus furnished with the sharpest possible test of the principle involved.

We come now to the third achievement of physical chemistry in the realm of pure chemistry. This has to do with the nature of the solutions of acids, bases, and salts. These have been called electrolytes, since they conduct electricity, and since the dissolved substance is decomposed into two so-called ions. At the one pole acids give hydrogen, while at the other (the positive) the rest of the molecule is set free.

This ion in the case of oxygen salts usually decomposes with evolution of oxygen. For example:

$$HCl = H + Cl \ ,$$
$$CuSO_4 = Cu + SO_4 \ , \quad \text{and } SO_4 = SO_3 + O \ .$$

The application of Avogadro's law as extended to solutions, especially dilute ones, has had curious consequences in the case of electrolytes. It appears that the number of dissolved molecules is greater than that corresponding to the smallest possible chemical formulæ, such as $CuSO_4$ or HCl in the above examples. This excess in the number of molecules forces us almost irresistibly to the belief in a genuine decomposition. In the case of salts, *a priori* considerations might lead us to the inference that in their solutions a mixture of the acid and base would be found. If this were the case no heat change would be perceptible when the acid and base in suitably diluted form were mixed, since no formation of salt should result. As a matter of fact, however, experiments show that a notable production of heat actually occurs. Then, too, this explanation is obviously inapplicable to the solution of an acid or of a base by itself.

A fortunate release from this dilemma was suggested by Arrhenius in the assumption of electrolytic dissociation. This assumption consists, as is well known, in the idea that the ions which are liberated when the solution is decomposed by electricity are all present in the free condition before the application of the current. Their presence is not perceived, in consequence of an electrical charge which is attached to them and which they lose during electrolysis. Thus, in dealing with hydrochloric acid, we can see that the dissolved body is not HCl, but a mixture of $\overset{+}{H}$ and $\overset{-}{Cl}$, that is to say, of positively charged hydrogen and negatively charged chlorine atoms. That these charges of electricity should so profoundly alter the behavior that neither the familiar properties of hydrogen nor those of chlorine are perceptible in the hydrochloric acid solution, appears at first sight to be a serious objection. On closer consideration, however, we see that this conception may be accepted as a possibility, even if the difficulties have not been completely cleared up. Over against this ground of hesitation we are in a position to set a great number of facts which before the assumption of electrical dissociation were without explanation. Not only so, but this theory has enabled us to foretell chemical occurrences and to some extent account for them mathematically. It may be added that Raoult, who has devoted himself for more than twenty years to the study of dilute solutions, at first rejected this theory, but now fully concurs in the explanation offered by Arrhenius.

If it is a question of facts of a qualitative nature, one has only to put forth his hand in any direction. Thus, chlorine as it is contained in electrolytes, such as solutions of hydrochloric acid and its salts, which according to this theory contain it in ionic form, behaves in an entirely different manner from the element as it is found in compounds of a different sort, like chloroform and chloral. The former with silver nitrate give silver chloride at once, the latter do not. Again, the identity in the color of the different salts of rosaniline, whether we take the nitrate, hydrochloride, or any other, finds its explanation at once in the presence of the same colored ion. The smallest change in this colored ion, however, by the introduction of methyl, for example, produces profound and much prized changes in tint. Still again, the equal optical rotations of solutions of the various salts of tartaric acid may be accounted for by the fact that they contain the same optically active ion, while a change in this ion itself, by the introduction of acetyl, for example, produces instantly a marked change in the extent of the rotation.

The results of quantitative measurement are not less convincing, although unfortunately always limited by the fact that the foundation of the calculations, the extended law of Avogadro, is strictly applicable only to the condition of extremest dilution. The limits of time forbid our pursuing the subject in greater detail in this direction. I simply mention the calculation of diffusion speed by Nernst, the calculation of the variation in the conductivity of distilled water with temperature by Kohlrausch, and the calculation of the influence of concentration on the behavior of organic acids and bases by Ostwald. A representative compilation of the achievements in this direction was presented by Arrhenius to the International Congress of Physicists, held at the Paris Exposition of 1900.

Finally, let me add that the liquid in which the life functions of living plants and animals are performed is invariably a dilute electrolyte. For this reason physiology and medicine have promptly taken possession of these new conceptions and the consequences even of their earliest applications have been most significant.

PHYSICAL CHEMISTRY AND INDUSTRIAL CHEMISTRY

LECTURE IV

PHYSICAL CHEMISTRY AND INDUSTRIAL CHEMISTRY[1]

The Co-operation of Physical and Industrial Chemistry—Two Illustrations to Be Discussed—Results of Scientific Study of Carnallite and Possibilities of Their Commercial Application to the Manufacture of Potassium Chloride—The Recent Discoveries in Connection with Alloys and Steel, Introduced by a Description of the Peculiar Behavior of Tin and its Explanation—White and Gray Tin and Their Transition Point at 20°—The Methods of Determining the Transition Point—Use of the Dilatometer—The Electrical Method.

In this and the' following lecture I purpose dealing with the application of physical chemistry to technical problems. In a general way, it may be said that since physical chemistry makes it possible to treat the problems of pure chemistry in a new manner with fruitful results, it follows almost of necessity that this influence of physical chemistry must be beneficial also to that branch of industry which is founded upon chemistry. It may be that in America the situation is different from what it is in Germany. Naturally I am insufficiently acquainted with the former, but I have been credibly informed during my stay here that in the industrial world the idea prevails that what can be done on a small scale in a laboratory experiment cannot be accomplished on a large scale in the factory. Of course there is naturally a difference between laboratory experimentation and technical investigation. In the laboratory it makes no difference whether the process pays or not, while this is precisely the most important question in the works. Aside from this, however, one may state with confidence that what occurs in a test-tube can also be done with hundredweights of material, provided the conditions, for example of temperature, are exactly imitated. The factory has, of course, resources so much beyond those of most laboratories that the imitation of laboratory conditions on a large scale is only a question of care. It is possible, however, that my informant did not reproduce the opinion in America on this point correctly.

---

[1] At the time this lecture was held, Knietsch's concise description of the contract process for the manufacture of sulphuric acid had not yet been given. I refer the reader therefore to his exceedingly interesting communication. *Ber. d. deutsch. chem. Gesell.*, Vol. XXXIV, p. 4069 (*cf.* also Sackur, *Zeitschrift für Elektrochemie*, Vol. VIII, p. 77).

There exists in Germany a very beneficial co-operation between laboratory work and technical work. Both go as far as possible hand in hand. After physical chemistry had made several important advances and was firmly established in such a way that pure chemistry was assisted by co-operation with it, Ostwald judged correctly that this co-operation would also be valuable in technical directions. In this belief about eight years ago he founded the Electrochemical Society, of which I happen at the present moment to have the honor of being president. I may add that in those eight years this society, whose chief object was to bring together the men of pure science and the representatives of technical science, has succeeded in gathering six hundred members. All the most conspicuous chemical industries of Germany and other countries are represented in the society.

The society possesses in addition its own organ of publication, the *Zeitschrift für Elektrochemie.* At the last general meeting in Freiburg in Baden the desirability of expanding the society was discussed in order that the co-operation between technical and scientific chemistry might not be confined to the territory of electrochemistry. It seemed possible to include physical chemistry as a whole, so far as parts of the subject other than this one had already found application or appeared to be capable of finding it.[1]

Nor has the stimulus to this co-operation its source purely on the scientific side. That it comes from both parties may be seen, for example, in the fact that a year ago Professor Goldschmidt, at that time the representative of physical chemistry in Heidelberg, was asked by the directors of the Badische Anilin- and Sodafabrik to give a series of lectures on this branch of the science before the chemists of the factory, and did so with great success. That an opening up of new points of view in the treatment of practical problems was expected to flow from these lectures rather than immediate practical results, is evident when we consider the present purely empirical treatment of problems affecting industrial chemistry. Ultimately, however, direct results of its influence must appear without fail.

In selecting for discussion industries in which the application of physical chemistry may be most useful, we turn naturally once more to the inorganic side. In this direction, as we have already remarked, physical chemistry is most easy to apply. In the first place I mention the treatment of the salts at Stassfurt, where the problem concerns the treatment of deposits which must be considered the results of the evaporation of sea-water. The substances concerned are the chlorides and sulphates of sodium, potassium, magnesium, and calcium. The study of these salts and of their solubility-relationships, recently resumed, and this time from the physico-chemical standpoint, may be expected to have some influence on their treatment for manufacturing purposes. In the second place we may name the field of metallurgy, particularly alloys and steel. The study of these subjects in the same fashion, as has been stated by those with authority to speak on the subject, is likely to lead to a new epoch in siderology. The practical applications of electro-chemistry, which are being developed at Niagara, and in an especial degree also the use of so-called catalyzers, that is to say, substances which increase the speed of reaction of chemical changes, like platinum in the new method of making sulphuric acid, likewise furnish an opportunity for the fruitful employment of physical chemistry.[1] A few examples will illustrate these possibilities.

---

[1] As the result of this discussion the society is now known as the "Deutsche Bunsen-Gesellschaft für angewandte physikalische Chemie." [A. S.]

Let us begin with the salt industry and linger for a moment once more to continue the discussion of carnallite, which has the composition $KCl \cdot MgCl_2 \cdot 6H_2O$, and is well known to be one of the most important commercial sources of potassium compounds.

The treatment of this double salt depends essentially upon the fact that, when the mineral is brought in contact with water, the magnesium chloride goes for the most part into solution, while the potassium chloride remains in the solid form. When the liquid has been saturated with carnallite the composition of the solution at 25° is expressed by the formula

---

[1] As the proofs of this work are being corrected I hear of the founding of an American Electrochemical Society, which according to the program of addresses has the object of assisting in such applications.

$$[1000H_2O + 11KCl + 73MgCl_2].^1$$

The action of water in this case, therefore, corresponds with the equation:

$$73(KCl\,.\,MgCl_2\,.\,6H_2O) + 562H_2O = [1000H_2O + 11KCl + 73MCl_2] + 62KCl\ .$$

When this saturated solution is concentrated, carnallite crystallizes out until finally chloride of magnesium begins to appear. At 25° this takes place when the composition of the solution has become

$$[1000H_2O + 2KCl + 105MgCl_2]\ .$$

The result of this concentrating process, therefore, is expressed by the equation:

$$[1000H_2O + 11KCl + 73MgCl_2] = 339H_2O + 9\ 8(KCl\,.\,MgCl_2\,.\,6H_2O) + 0\,.\,6[1000H_2O + 2KCl + 105MgCl_2]\ .$$

The final liquid is thus essentially a solution of magnesium chloride. The carnallite which has crystallized out can be treated with water as before. The disposition of the magnesium chloride mother-liquor, so as to avoid the contamination of river waters, appears to be a problem of no little difficulty.

---

[1] In what follows, symbols representing the composition of solutions are placed within square brackets

The re-examination of the carnallite problem from the physico-chemical standpoint, which we have discussed in the previous lecture, possesses the advantage that it shows at one glance all the possible methods of splitting carnallite. The one just referred to takes its place as a special case. As a result of this more general treatment, however, two other processes emerge and are to be considered as possibilities, even in the matter of technical application. One of these is founded on a transformation of carnallite in which, below $-21°$, it takes up water and forms potassium chloride and the dodecahydrate of magnesium chloride. Working under these conditions the reproduction of about 14 per cent. of the original carnallite which occurs in the process at present in use would be avoided. After saturation with carnallite and separation of potassium chloride, a solution would be formed of the composition

$$[1000H_2O + 10KCl + 66MgCl_2] .$$

From this, by concentrating or cooling, magnesium chloride with twelve molecules of water of crystallization and potassium chloride would be deposited. A second possibility of obtaining potassium chloride is indicated by the decomposition of carnallite at 168°. In this case three-quarters of the potassium chloride is separated, and one-quarter, with all the magnesium chloride and water, may be poured off in fluid form. The operation must of course be conducted in closed vessels, since the pressure of the water of crystallization in carnallite at 168° is greater than one atmosphere. If this liquid is separated from the solid potassium chloride by some sort of filter press, and is lowered in temperature to 115°, the potassium chloride still contained in it reappears in the form of carnallite. The hot solution now remaining can again be separated from the solid by pressure, and is an almost pure, melted hydrate of magnesium chloride, free from potassium compounds.

In the technical point of view a good deal may be said in favor of the last process. A decomposition of the carnallite (without the formation of any mother-liquor) takes place, in the course of which three-fourths of the potassium chloride as such and, in the final step, a corresponding amount of solid magnesium chloride are obtained, while a quarter of the carnallite is recovered unchanged and can be worked up afresh. Thus, what in the ordinary process is attained by the use of a solvent and by taking advantage of solubilities is here reached by changes in temperature and the accompanying phenomena of transition or of melting and solidification. How far, however, a remunerative process is involvod in this can be shown by future study only. So much we know, that the operation as it may be carried out in the laboratory with a few grams has also been found to work in the factory when several kilograms are used. The applicability of the method on a large scale is thus assured, as we might have expected. The question of cost alone remains open.

As a second example, I desire to discuss the application of physical chemistry in the field of metallurgy. By far the most important illustration in this direction is in connection with the manufacture of steel and the explanation of its peculiarities. Authorities in this subject admit on all hands that physical chemistry has thrown a most welcome light on the complicated phenomena presented by the behavior of steel. These of course primarily depend upon the interactions of iron and carbon. The interactions, however, are complicated by the fact that transformations occur both in the iron and in those constituents which contain both carbon and iron. It will simplify the matter greatly, therefore, if we first consider the changes which occur in a single metal. We may take tin as being the metal in connection with which changes of this kind have been most completely investigated.

The remarkable fact in the behavior of tin to which I ask your attention was discovered long ago. Careful historical investigation has demonstratod that even Aristotle was acquainted with the fact, whose explanation has so recently been brought to light. The fact referred to is that common tin is capable of undergoing a profound change which amounts to a complete disguise. The product of this change, for reasons which we shall learn later, cannot be exhibited to you, and I must therefore content myself by showing a photograph of a piece of tin which is undergoing this transformation (Fig. 4). The impression which examination of this piece of tin makes is that of an object which has been overtaken by some disease. As a matter of fact, indeed, the phenomenon has this in common with disease, that it is contagious. When the phenomenon exhibits itself, as it sometimes does, in the pipes of church organs, it is consequently a good plan to remove the objects which have become infected. The disintegration into a gray powder, which marks the progress of the attack, proceeds gradually until, especially in the case of thin bodies like organ pipes, the object has been completely destroyed. We must not delay to add that, in spite of appearances, the change is not due to the influence of the atmosphere or its moisture. On the contrary, the tin undergoes the change all by itself, and the gray product has only to be heated in order that without change of weight it may be reobtained in the original metallic form It is precisely on account of the influence of heat on the change that, at the temperature which we are at present experiencing, I am unable to show this so-called gray tin.

We owe particularly to Schaum[1] and Cohen[2] our knowledge of the conditions which influence this extraordinary change. The conclusion is that the whole phenomenon is related to a definite temperature, namely 20° C. Below this temperature the formation of gray tin can occur, while only above this temperature is the formation of the common variety possible. The temperature limit 20°, commonly known as the transition point, separates two ranges of temperature in which the gray and the white tin respectively are stable. It exhibits thus a certain analogy to a melting-point, with this sole difference that at a melting-point a so-called change of state occurs. In the latter case the bodies are solid and liquid respectively. The temperature 0°, for instance, can be named the transition point of ice and water. Along with this analogy between the two kinds of phenomena, which by the way were compared even by Aristotle, one striking difference is to be noticed. This difference probably accounts for the fact that the limiting temperature of 20°, which separates gray from white tin, was not discovered until the new methods of physical chemistry became available. This notable difference lies in the extreme slowness of the change in the case of tin. Indeed, the change may fail to put in an appearance for years. In the case of ice and water, on the other hand, superheating of ice even for a moment seems to be impossible, and although overcooling of water beyond 0° can occur, the slightest touch with ice destroys the overcooling instantly, and causes freezing. In the case of tin almost every possible means must be used to bring the change about, at all events when the temperature of experiment is not too far removed from 20°.

---

[1] *Liebig's Annalen*, Vol. CCCVIII, p. 29.

[2] *Zeitschr. f. physik. Chem.*, Vol. XXX, pp. 601, 623.

If this reluctance to change did not exist, the temperature of transformation could be observed like a melting-point. It could be followed with the assistance of a thermometer, for, in close analogy to the phenomenon of melting, the formation of white from gray tin is accompanied by the disappearance of heat. The extreme slowness of the process, however, renders the employment of other means necessary. I shall describe two of them. Before doing so, however, I should remark that delayed processes of this kind are in general more common in connection with chemical transformations than in physical changes of state, even though the latter are often closely analogous to the former.

One of the methods makes use of the very notable change in volume which accompanies the transformation of the tin.

Ordinary tin has a specific weight of 7.3, while in the case of gray tin this constant has the value 5.8. Thus, white tin expands more than a quarter in undergoing the change. An alteration in volume like this can be very easily studied by the help of a dilatometer. This instrument is a kind of thermometer of rather large dimensions. Its reservoir is packed with the substance under investigation—in this case the tin. After the reservoir, which originally was open for the reception of the contents, has been closed, the air is pumped out, and a suitable liquid is admitted. The changes in the level of this liquid in the capillary tube serve as an indication of the alterations in volume which occur in the contents of the reservoir, and can be read off with the help of a scale. Without special precautions, however, the object could not be attained by these means alone, since, without stimulus, the transformation often fails altogether to occur. The chief among the necessary conditions is that both kinds of tin intimately mixed should be introduced into the instrument. This intimate contact serves to stimulate either transformation, so that the sensitiveness of the arrangement is greatest when equal quantities of the two bodies are present. An additional expedient is indispensable in the present case. The liquid used for filling the apparatus must be capable of dissolving to the greatest possible extent the body which is undergoing the change. A solution of pink-salt ($SnCl_4 . 2NH_4Cl$) has been found most suitable. The tin dissolves in this substance with the formation of stannous chloride. That one of the two transformations which under the given conditions tends to occur, is brought about through mediation of this process of solution. One modification dissolves and the other is deposited. Working in this fashion the dilatometer, when kept at a constant temperature, shows the transformation in one direction or the other in admirable, if somewhat leisurely, fashion. For example, a gradual increase in volume, which may continue for days, is observed at 19°. On the other hand, a slow contraction occurs at 21°. At 20° the system remains at rest, and thus the transition temperature is determined within one degree.

While applications of the method the description of which we have just concluded always occupies several days or even weeks, a second plan, which is now to be mentioned, has the great advantage that the determination of the transition temperature can be made in a short time and with much greater accuracy. The second method makes use of the electrical currents which under suitable circumstances are produced by the transformations of the two forms of tin. The apparatus itself is again very simple. It consists of two short, rather thick-walled test-tubes, which are connected by a siphon or a cross-piece opening into the side of each. In one of the tubes some gray tin is placed, and in the other some white tin. Metallic contact with the material is made by means of two platinum wires fused into the bottoms of the test-tubes. These form the poles of a cell and are connected with a very delicate galvanometer. The circuit is closed by means of pink-salt solution, with which the two test-tubes and the siphon or cross-piece are filled. When the temperature is not far from 20° a direct transformation of the specimens of tin does not occur. The only consequence of the tendency to change is that on the one side the modification which is unstable at the existing temperature passes into solution, while the metal in the other test-tube increases by deposition. Since, however, this deposition can occur only with the assistance of the positive ions of tin, the mass of tin which is increasing in quantity acquires a positive charge, while the other, which is furnishing positive ions to the solution, is losing an equivalent charge. The current which is produced in this fashion, and whose existence and direction may be foretold, can actually be observed. In consequence of the delicacy of electrical measurements, it furnishes a very exact indication of the direction in which the transformation is proceeding. The formation of the gray tin produces a current in one direction, that of the white in the opposite direction. The transition temperature is indicated by a reversal of the poles.

LECTURE V

PHYSICAL CHEMISTRY AND INDUSTRIAL CHEMISTRY

Results of the Physico-Chemical Study of Wrought Iron, Cast Iron, and Steel—Complications Introduced by the Presence of Carbon and by the Occurrence of Solid Solutions—Method of Studying Iron by Polishing, Etching, and the Use of the Microscope—Constituents are Ferrite, or Pure Iron; Martensite, or the Solid Solution of Carbon in Iron; Cementite, or the Carbide of Iron, Graphite, or Free Carbon; Pearlite, or the Cryohydratic Mass—Two Forms of Ferrite with Transition Point at 850°—Pearlite, a Mixture of Cementite and Ferrite, and its Formation and Composition—Hard Steel is Overcooled Martensite—The Graphite—The Behavior of Melted Iron Rich in Carbon—Rapid Cooling Gives White Cast Iron Containing Much Cementite—Slow Cooling Gives Gray Cast Iron by Decomposition of the Cementite and Production of Graphite, and Finally Pearlite—A Numerical Illustration of the Behavior of Molten Iron Containing 6⅔ per Cent. of Carbon When Cooled (1) Rapidly and (2) Slowly.

I SHOULD like to employ the second hour which is to be devoted to the application of physical chemistry to technical chemistry, in giving you some conception of what it has done for the study of iron. Under this term we include not only wrought iron, but also cast iron and steel, which are forms of iron containing more or less carbon. I would call your attention first to the fact that von Jüptner, one of the most noted authorities on steel, has described the results of this study as establishing an epoch in the iron industry. In recognition of this, his recent work on siderology is furnished with an introduction of sixty-one pages dealing with the laws of solution.

The behavior of steel in particular is far from simple, and so yesterday I prepared for the introduction of this subject by explaining the simpler but somewhat analogous behavior of tin. Tin, like iron, is a metal, but, while in the case of the former we have a single substance occurring in different modifications, when we approach the study of the forms of the latter which are of technical importance, we find that the carbon which is present plays a very important part In spite of this complication, the new physico-chemical method of treating such problems has illuminated successfully a rather confusing set of phenomena. It has made it possible to represent the whole behavior of carboniferous iron by means of one diagram, inspection of which enables us to grasp the essential features at one glance.

A second introductory explanation is necessary. In the case of tin, the peculiar occurrence of a metal in different forms and the laws governing the transformation of these were emphasized. In the case of iron in its different conditions this phenomenon recurs, but a second, consisting in the appearance of so-called solid solutions, has also to be noticed.

The grasp which we have obtained of the nature of ordinary fluid solutions has been so fruitful and its influence so far-reaching that the attempt has been made to proceed one step farther and to apply the same conceptions to substances in the solid condition. We are certainly entitled to speak of solid solution in certain definite cases, where the complete homogeneity combined with the possibility of varying composition, which are characteristic of the state of solution, are found. In colored specimens of glass and in isomorphous mixtures, of two alums for example, we are just as little able, even with the help of the microscope, to perceive the presence of more than one substance, as in a solution of sugar in water. It is a familiar fact that the ordinary colorless alum, when crystallizing from solutions containing the highly colored chrom-alum, forms octahedra, more or less tinted with chrom-alum. And yet the most minute observation reveals no gross irregularities in the physical distribution of the material, or any other evidence of lack of homogeneity. In such a case, therefore, we speak of the existence of a solid solution. When the substance is amorphous, as in the case of colored glass, the analogy to a fluid solution is so complete that the two are connected by a series of more or less viscous mixtures in such a way that no sharp distinction can be drawn. Of course, when the solid solution is crystalline it must be admitted that it differs from a fluid solution fundamentally, in so far that an arrangement of the molecules according to some definite order has taken place.

The essential point is that the laws of fluid solutions have been successfully applied to solid ones,[1] and that this application has thrown light upon the behavior of varieties of iron containing carbon.

Passing now from these preliminary statements in regard to tin and solid solutions, let us take up the main subject. The first thing to be noticed is that, while in the case of tin only two forms had to be considered, there are here more than two. In the industrial point of view there are three forms of iron—wrought iron, steel, and cast iron—which differ from one another by containing proportions of carbon increasing in the order given. Obviously, too, the proportion of carbon is not the only thing to be considered. This is demonstrated by the change produced by chilling and hardening steel, which results from more or less rapid cooling following upon elevation to some definite temperature and occurs without any alteration in composition. On this account the investigation of iron demands not only analysis but also microscopic study. The specimen is first polished and then etched by the use of a solution of hydrogen chloride in alcohol. Sometimes continued polishing with emory and a plate of rubber is employed to secure a slight elevation of the harder parts above the more easily abraded, softer places. In either case, such a specimen, when studied microscopically so that the light falls upon it obliquely, shows peculiarities of structure which permit of further differentiation of the constituents. As a result of this we speak of ferrite, which is pure iron, of martensite, which is carboniferous iron of varying composition but homogeneous structure (the solid solution), and of cementite, a compound of iron and carbon corresponding to the formula Fe_3C. Besides these, pure carbon in the form of graphite, and sometimes of diamond, is discoverable. A fifth constituent is pearlite, a carboniferous iron, heterogeneous in structure, but possessing a constant composition. It may be that still other forms should be discriminated, but their existence has not yet been determined with perfect certainty.[1]

---

[1] BRUNI, "Über feste Lösungen;" AHRENS, *Sammlung chemisch-technischer Vorträge*, 1900.

---

[1] BAKHUIS-ROOSEBOOM, *Zeitschr. f. physik. Chemie*, Vol. XXXIV, p. 437, BENEDICKS, *ibid.*, Vol. XL, p. 545; STANSFIELD, *Journal of the Iron and Steel Institute*, 1900, Vol. II.

Beginning with pure iron (ferrite), I mention first a fact determined by Le Chatelier. He found that, like tin, iron exists in two forms, whose transformation is dependent upon a definite temperature, which in this case is 850°. These two forms we shall distinguish as α-ferrite and β-ferrite. That which is stable in the cold, and in general below 850°, is α-ferrite. Soft wrought-iron which has been freed as far as possible from carbon, as, for example, piano-wire, is of this kind. We record this first fact in the diagram, Fig. 5, in which the temperature is read along the axis of abscissæ and the content of carbon along the axis of ordinates.

The second fact which must be noted is that β-iron is capable of taking up carbon in solid solution, while α-iron does not possess this property. Recalling the analogy between transition temperatures and melting-points, and the additional conception of solid and fluid solutions, we perceive that the addition of carbon to β-iron will depress the temperature of transformation, just as dissolved substances lower the freezing-point of melted bodies. Von Jüptner has even applied the laws of fluid solutions to calculation of the extent of this depression. Graphically this depression is expressed by a line proceeding from the point 850° on the horizontal axis and ascending to the left in correspondence with the lowering in temperature and increasing content of carbon.

Just as a melting-point cannot be depressed without limit by the addition of soluble substances, so is it with the transformation temperature of a solid solution like this. As the solvent gradually freezes out of a fluid solution, the proportion of the dissolved body in the mother liquor increases until finally the solute also comes out in some

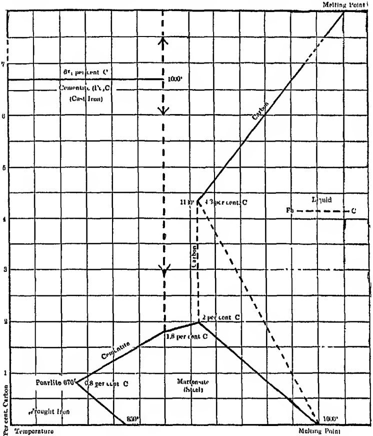


FIG 5

C = Carbon (Graphite and Diamond). Fe = Iron (α- and β-Ferrite)

form (for example, as a solid). When this occurs, the lowest freezing temperature has been reached, and at this temperature the rest of the mass assumes a solid condition. This mass is not homogeneous; it has a definite composition, namely that peculiar to the solution at the lowest temperature of freezing. The solid solution of carbon in iron behaves analogously. The carbon content of the solid solution increases as ferrite is deposited, until it reaches 0.8 per cent. From this the carbon now begins to separate at 670° in the form of cementite (Fe_3C). In the case of solutions, the complex or conglomerate material, produced by the freezing of the solution saturated at the lowest temperature of freezing, was formerly regarded as a single substance on account of its definite composition. In the case of aqueous solutions it was named a cryohydrate. The same thing was done in the present case and the product was called pearlite. Its true nature, however, has now been brought to light in the present case also, and the constancy of its composition is explained. It is a complex of ferrite and cementite. It corresponds to a slowly cooled steel containing 0.8 per cent of carbon. It may be compared with special aptness to the cryohydrate of a salt, which, like sulphate of copper, occurs in the cryohydrate in the form of a true hydrate. In this the ice corresponds to the iron and the hydrated sulphate of copper to the carbide of iron. Taking a cryohydrate which solidifies at $-5°$, we may express the analogy diagrammatically as follows:

$$\underbrace{\text{Cryohydrate}}_{\text{Ice} \qquad \text{Hydrate}} \overset{-5^\circ}{\leftrightarrows} \text{Solution}$$

and

$$\underbrace{\text{Pearlite}}_{\text{Ferrite} \qquad \text{Cementite}} \overset{670^\circ}{\leftrightarrows} \text{Solid Solution}$$

All the phenomena we have described in both these cases announce themselves in precisely the same manner when a thermometer is employed. The only difference is that in the case of the solution the progress of the changes can be observed with the eye, while in the case of iron the final investigation of the structure is required to enable us to ascertain that when 0.8 per cent. of carbon is present pearlite is formed, and when less carbon is present ferrite and pearlite are found together.

What will happen with forms of iron with larger proportions of carbon may again be anticipated by comparison with the behavior of a solution. A solution which contains more sulphate of copper than corresponds to the cryohydrate deposits, when cooling, first cupric sulphate and then the cryohydrate. In precisely the same way iron with a higher proportion of carbon gives first cementite and then pearlite.

That this analogy is supported by the facts to so great an extent is due to an entirely unexpected property of these solid solutions of carbon in iron. This property consists in the fact that in spite of the solid condition of the substance an internal separation can occur. This must be accompanied by spatial displacements which can be produced only by movement. Internal mobility like this, however, must become less with diminished temperature, and in this fact we have the explanation of the property which steel has of assuming either the hard or the soft condition. When the cooling is rapid, the separation we have just mentioned is passed over, and, of course, does not take place in the mass once it becomes cold. The solid solution remains a solid solution, and the substance is in this case hard steel (martensite). It may be added that the theory of solution is not entirely unable to account even for this increase in the hardness of iron when carbon is contained in it in a state of solid solution. In explanation of this it may be suggested that a dissolved substance lowers the vapor tension of a pure solvent, and therefore in solids exerts an influence against the abrasion of the surface.[1] According to the proportion of carbon these solid solutions form a continuous series from the soft, pure iron to the very hard cementite.

We have still a third phenomenon to explain, namely, the well-known separation of carbon as graphite, which frequently occurs in iron. This brings us back to the forms of the substance which are rich in carbon. If we start with cementite (Fe_3C), which corresponds approximately to the white cast iron of industry, we find that a separation occurs in this compound above 1000°. From it graphite and a solid solution containing 1.8 per cent. of carbon are produced. This temperature and this particular proportion of carbon thus form the limits for those kinds of iron which, when slowly cooled, produce cementite. We can unite this point (Fig. 5) with the one representing 0.8 per cent. of carbon at 670°. When this is accomplished the study of that part of the phenomena which is connected with the transformation of a solid solution is almost exhausted.

Let us now turn to the material in a state of fusion, that is to say, to the liquid solutions, and begin with pure iron and its melting-point, 1600°. This point we place on the diagram upon the horizontal axis. From this point proceeds the curve of melting temperatures as they are depressed by the addition of carbon. The line ends at the iron of lowest melting-point, which contains 4.3 per cent. carbon and melts at 1130°. In consequence, specimens of iron containing more carbon, when slowly cooled, deposit even at temperatures above 1130° the excess of carbon beyond 4.3 per cent. which they contain. From the fused material containing 4.3 per cent., as Roozeboom has pointed out in describing an investigation of other solid solutions and the fused masses corresponding to them, no solid solution with an equal amount of carbon is formed. The solid solution contains only 2 per cent., while the other 2.3 per cent. turns into graphite (under high pressures, diamond). This point is the termination of the series of solid solutions which begin at 1000° with 1.8 per cent. carbon, and when slowly cooled deposit graphite. In the diagram these two points are thus connected by a line.

---

[1] BARUS, *Wied. Ann.*, Vol. VII, p. 383; Vol. XI, p. 930.

Finally it must be added that in the melted material also separation may fail to occur when the cooling is rapid, and so from a melted substance having, for example, the composition Fe_3C, cementite in large leaf-like crystals, that is to say, white cast iron, may be obtained. On the other hand, when the cooling is slower, graphite will first appear, then cementite, and finally pearlite, and the resulting mixture is gray cast iron. The diagram thus represents the stable conditions which are reached when the cooling is slow.

If we now turn to the diagram for answer to definite questions we find that it is sufficient simply to place upon it the initial condition as defined by the percentage of carbon and the temperature. The phenomena which will appear as the mass cools may then be traced by going horizontally to the left until one of the lines is encountered. This line will indicate a separation of some definite nature during which we follow the direction of the line itself. Rapid cooling, on the other hand, corresponds to an uninterrupted movement to the left. It probably will be most interesting to trace the behavior of a mixture of $6\frac{2}{3}$ per cent. carbon with $93\frac{1}{3}$ per cent. iron (corresponding to Fe_3C), beginning at 2000° (that is to say, starting from the melted condition), and noting the result of each kind of treatment. If the cooling is rapid cementite is formed. If the cooling is slower, carbon in the form of graphite is first to be expected. The amount of this can be calculated, since iron at 1130° containing 2 per cent of carbon will remain, and this in turn in passing down to 1000° will sustain a further separation of graphite until iron with 1.8 per cent. of carbon remains. The amount of graphite separated from the original 100 parts of iron is obtained by calculation, thus:

$$6\tfrac{2}{3} - \frac{93\frac{1}{3}}{98.2}1.8 = 4.96\ .$$

The remaining 95.04 parts of iron containing 1.8 per cent. of carbon now deposit x parts of cementite containing $93\frac{1}{3}$ per cent. of iron, until at 670° the percentage of carbon has sunk to 0.8. The remainder $(95.04 - x)$ yields pearlite with 99.2 per cent. of iron. Thus the 93.3 parts of iron are divided as follows:

$$93\tfrac{1}{3}=\frac{93\frac{1}{3}}{100}x+(95.04-x)\frac{99.2}{100}\,.$$

Solving this equation we find $x=16$.

Collecting these results we find that 100 parts of the original substance (containing $6\frac{2}{3}$ per cent. of carbon) yield when slowly cooled approximately five parts of graphite, 16 parts of cementite (containing $6\frac{2}{3}$ per cent. of carbon), and 79 parts of pearlite (with 0.8 per cent. of carbon).

PHYSICAL CHEMISTRY AND PHYSIOLOGY

LECTURE VI

PHYSICAL CHEMISTRY AND PHYSIOLOGY

The Theory of Solutions Based upon the Extension of Avogadro's Principle and its Importance in Physiology—Osmotic Pressure and Osmotic Phenomena—The Experiments of de Vries with Plant Cells—The Work of Donders and Hamburger with Blood Corpuscles—The Experiment of Massart with the Human Eye and with Bacteria—Loeb's Work on Artificial Fertilization—The Measurement of Osmotic Pressure—Observation of the Freezing Points for Determining Equality of Osmotic Pressure—Specific Action of Ions in Physiology.

If you refer to our program you will find that it was my intention next to devote two lectures to the relation of physical chemistry to physiology.

By way of introduction let me recall the statement that the recent development of physical chemistry rests, so to speak, upon two foundation stones. One of these is usually known as the theory of solution, and depends essentially upon the extension of Avogadro's principle to solutions. The other is the application of thermodynamics, and especially of the Carnot-Clausius principle, to chemical problems.

In physiology the theory of solutions finds particular and indeed almost exclusive application. The thermodynamics may be left out of account. That this theory has assumed special significance in the science of physiology is principally due to two factors, which must now be set forth.

As we have already mentioned, the new application of Avogadro's law, just like the original one, applies strictly only to the condition of infinite dilution. Nevertheless, its practical application to gases at the ordinary pressure and to solutions of the strength known as deci-normal may be carried out without serious misgiving. Now it is a fortunate circumstance that in the region of physiology the processes which have to be considered all take place in just such dilute solutions.

To this we must add a second factor. The new theory of solution finds its simplest expression in application to osmotic pressure. In this form it states that, when the concentration is low, at equal temperatures and concentrations osmotic pressure and gaseous pressure are equal, and that they vary according to the simple laws of gases. Now it is a fortunate accident that this very osmotic pressure, which has recently become accessible to calculation and quantitative study, plays a conspicuous part in the physiological processes both of animals and of plants. Its significance has become more and more apparent of recent years, and the literature of the subject has already become very comprehensive.

The words of Loeb, uttered a few years ago in a lecture on "The Physiological Problems of Today," delivered at Ithaca, recur to my mind (p. 11). I recall particularly the final reference of the author to the fact that, since the period immediately following the discovery of the law of the conservation of energy, the outlook for progress in physiology has never appeared brighter than at present. For opening up this prospect the theory of solutions is undoubtedly primarily responsible. Other writers have since then expressed themselves in the same way.[1]

I may add also that just as the relation of physical chemistry to technical chemistry has led to Goldschmidt's series of lectures before the employees of the Badische Anilin- und Sodafabrik, so its relation to physiology and medicine has produced a series of addresses by Cohen before the physicians of Amsterdam. German and English translations of these lectures have now appeared.[2]

As regards details, I shall take as my starting-point a brief survey which I presented in 1891, on an occasion similar to this, in Utrecht. At that time everything was still in an incipient stage. Even then, however, the investigations of de Vries[3] on the growth of plants were of fundamental importance. In connection with this the mechanism of the extraordinary tension which distinguishes growing plants, and is absent in withering ones, was studied. The question is one of absorption of water in the former case and of loss of water in the latter. This function, however, is accomplished by means of a definite cell constituent or organ, whose work may best be observed in plants which, like *tradescantia discolor*, have a colored cell content. When withering is artificially produced by dipping the cell in a sufficiently concentrated salt solution, water tends to be abstracted. The microscopic investigation shows that in each cell an elastic skin with colored contents, which usually fills the whole cell, becomes separated from the cell wall and suspends itself like a sphere in the interior. On the other hand, this so-called protoplast expands when the salt solution is replaced by water. It soon fills and ultimately stretches the cell. When this condition arises cell division and growth become possible. Obviously, substances which attract water, like sugar, salts, and vegetable acids, must exist, dissolved in this protoplast, and indeed their presence may be demonstrated. At the same time, and this is essential for a behavior such as we have described, the elastic membrane must permit the passage of water, but not that of the substances just mentioned which are dissolved in the cell sap. In the contrary case, these substances would soon diffuse out and the protoplast would lose its ability to lend to the plant this tension or turgor which is essential for development.

---

[1] Hamburger, *De physische scheikunde in hare beteekenis voor de geneeskundige wetenschappen*, Groningen, 1901. See also His, *Die Bedeutung der Ionentheorie für die klinische Medizin*, Tübingen, 1901.

[2] Cohen, *Physical Chemistry for Physicians and Biologists*, translated by Dr. Martin H. Fischer. New York: Henry Holt & Co., 1903. The significance of the determination of freezing-points has been treated also by Rosemann, *Die Gefrierpunktsbestimmung und ihre Bedeutung für die Biologie*, Greifswald, 1901.

[3] "Eine Methode zur Analyse der Turgorkraft," *Pringsheim's Jahrb.*, Vol. XIV.

Here we encounter the so-called semipermeable membrane which is ideal for the exhibition of an osmotic phenomenon, and was presently used by de Vries for the measurement of osmotic forces. It appeared that two different solutions which exerted the same osmotic influence upon the protoplast possessed the same osmotic pressure. Ability barely to separate the protoplast from the cell wall was taken as an indication of the presence of this tendency in equal degree. Equality was considered to exist when in some of the cells, but not in all, the separation from the polyhedral cell wall could just be observed through the microscope. Thus two facts were ascertained. The first was that the osmotic pressure of the cell content, or, as we prefer to call it, of the content of the tonoplast, brings about growth. The second was that plants furnish a means of determining when solutions are isotonic, or, in other words, when their osmotic pressures are equal.

A second series of experiments dealing with the animal organism was soon ranged alongside of those connected with plant physiology. It was carried out by a renowned physiologist, Donders, in association with Hamburger.[1] These investigators found that the behavior of the blood, or more exactly of the red blood corpuscles, is closely connected with the osmotic pressure of the surrounding fluid. The phenomena observed may be briefly described. The blood is first defibrinated, that is to say, a part of the albumin, which disturbs the experiments by coagulation, is removed. The remaining fluid still contains the red blood corpuscles and presents the appearance of a red liquid. When this is placed in solutions, like that of sodium chloride, of varying concentrations, two different phenomena may be presented according as the concentration is great or small. In the dilute solutions the blood corpuscles lose their coloring matter and are thus deprived of the constituent which is essential to the performance of their specific function. In concentrated solutions they retain the coloring matter, but soon sink to the bottom of the colorless solution of the salt. On setting out to determine the limiting concentrations for various dissolved substances one would naturally expect that some specific influence of the dissolved body would be responsible for this action upon the blood corpuscles. It was therefore a matter of surprise to discover that here again the osmotic pressure was the sole controlling factor, and that the concentration correspondences, ascertained with this material, coincided exactly with those brought to light by de Vries' experiments with plants.

---

[1] *Onderzoekingen gedaan in het physiologisch laboratorium der Utrechtsche Hoogeschool* (3), Vol. IX, p. 26.

It may perhaps be permissible to refer to a series of experiments of an entirely different nature, or at least undertaken with an entirely different object. In them the human eye was the subject of experiments made by Dr. Massart[1] in Lüttich. He introduced into the eye, presumably his own, harmless solutions which had previously been warmed to the temperature of the body. Under these circumstances it was noted that when the solution was diluted beyond a certain limit the eye did its best to increase the concentration of the solution by evaporation. An unconquerable inclination to keep the eye open or to separate the eyelids was experienced. On the other hand, when the concentration of the solution exceeded a certain limit, the eye shut of its own accord. Evaporation was prevented, and the formation of tears brought about the necessary dilution. Here again the limiting concentration for bodies of the most different nature was determined, and the same relation was discovered between these solutions as had been noticed before in the experiments with red blood corpuscles and plant cells.

---

[1] *Archives de biologie Belges*, Vol. IX (1889), p. 15.

We may conclude the list of our illustrations, now that we have included in it experiments with the highest organism, by introducing something of a precisely corresponding nature in the case of the very simplest forms of life. The author[1] just mentioned has found that bacilli and infusoria are also sensitive indicators of this limiting osmotic pressure. The bacilli are placed under a cover-glass on the stage of a microscope. When bouillon is offered to them in a microscopic capillary tube they move into it as soon as they notice its presence. The prepared bouillon, however, contains a dissolved substance whose concentration is varied from experiment to experiment. Some organisms like *polytoma uvello* are not diverted by this from moving along the capillary, but they are killed sooner or later according as the concentration exceeds a certain limit to a greater or less extent. Other organisms, like *Bacillus megatherium*, do not enter the capillary if danger of destruction threatens them, but remain at the entrance to it. As the result of experiments with different substances a series of isotonic concentrations just like the preceding ones is obtained.

I shall not further occupy your time with illustrations of this kind. I merely refer to the fact that the above data, striking as they are, were collected more than ten years ago, and that in the intervening period similar things have been discovered in increasing numbers. A complete account of the literature of the subject was given a year ago by Koeppe.[2]

---

[1] See also WLADIMIROF, *Archiv fur Hygiene*, Vol. X (1891), p. 81.

[2] *Physikalische Chemie in der Medicin* See also COHEN, *Physical Chemistry for Physicians and Biologists.*

Since then, however, our interest has been attracted to the same subject by Loeb's discovery[1] that osmotic pressure can partly replace the act of fertilization of the eggs of sea-urchins. These eggs, which are laid in sea-water, die when they remain unfertilized. They begin to develop, however, if a temporary elevation in the osmotic pressure of the sea-water is produced by the addition of substances of the most varying characters, such as magnesium chloride, potassium chloride, sugar, and urea. The development, more particularly the cell division, proceeds until the organism begins to have powers of movement. It may be added that the discoverer, as might have been expected, thought at first that a specific action of the foreign material was responsible for the effect. This conception arose when chloride of magnesium was the only substance that had been tried. Later, however, when entirely different substances were found to have the same effect the osmotic explanation suggested itself. I may add also that this discovery, when presented to the American public without the osmotic conceptions connected with it, made such an impression that Loeb was heralded in the newspapers as the discoverer of the elixir of life. Loeb was himself probably the first to protest against these statements, but, as some suggestion of truth is generally to be found in newspaper articles, so here the report was a somewhat exaggerated expression of the entirely unexpected intrusion upon life phenomena which physical — in this case especially osmotic — action had permitted.

---

[1] *American Journal of Physiology*, Vol. III, p. 434; Vol. IV, pp 178, 423. I may add that the mechanism of fertilization, as this was explained by Boveri at the Hamburg Naturforscherversammlung (1901), seems, as I pointed out at the time, to represent in many ways an osmotic process produced by coagulation of albumen.

After it had been shown in so many different ways what a fundamental part osmotic pressure plays in physiological functions the question of the measurement of this pressure became a pressing one. Unfortunately osmotic pressure is susceptible of direct measurement only with difficulty. We have indeed succeeded in a few cases, particularly in consequence of the efforts of Pfeffer, in measuring this pressure directly. Without any doubt we shall some day be able to do it in all cases, but so far an easily applicable method has not been discovered. Nevertheless, this want can be almost entirely supplied in consequence of the relation which thermodynamics shows to exist between osmotic pressure and the depression of the freezing-point. This relation again holds only for dilute solutions. We know that solutions freeze at a temperature lower than the solvent. Thus sea-water freezes a considerable distance below 0°. We may even predict by calculation that a solution which exhibits an osmotic pressure of one atmosphere at 0° will freeze at −0.084°. The two values are proportional to one another in the case of dilute solutions such as exist in living organisms. It would be hard to find any other region in which several different branches of science—in this case, mathematics, physics, chemistry, anatomy, and physiology—have joined hands over the same problem. Here physiology required the determination of the osmotic pressure, and experimental determinations necessary for its theoretical deduction had been carried out by Raoult, Eyckman, Beckmann, and others. In any case, the absolute dimensions of the osmotic pressure do not usually require to be known. What we need are the relative values, which are given directly by observation of the depressions of the freezing-point. Equality in osmotic pressure, which is often so important in physiology, may be inferred directly from identity in the freezing-points.

One important conclusion from these investigations is that in the organism as a whole the most different liquids must be in osmotic equilibrium with one another and must therefore possess the same freezing-point. The same must be true of the more complex case of mother and child before birth. A notable exception is found in the secretions of the kidneys, which may sometimes exhibit abnormally high osmotic pressure. Anomalies of this kind may be indicative of diseases of the kidneys and of the heart, which is so closely related to them in its functions. Again, in certain cases, such as, for example, when one kidney is to be removed, the normal behavior of the other can be determined in advance by freezing-point measurements.[1]

It would not be advisable for me to linger any longer in this entirely foreign territory. I turn, therefore, to another conception still related to physiology which has been suggested by the co-operation of physical chemistry. This is connected with electrolytes.

As we have already had occasion to mention, the new conception of solutions, and especially of dilute solutions, forces us to the belief that in electrolytes an actual splitting of the dissolved substance has occurred. Such are the solutions of acids, bases, and, particularly, salts. The dissociation leads to the formation of so-called ions which are liberated during electrolysis. In this way chloride of sodium, for example, is held to contain in its solution positively charged sodium and negatively charged chlorine. The physical properties are in harmony with this theory, and indeed render it almost inevitable, since the osmotic pressure has nearly double its normal value. The most various chemical properties are also explicable by this assumption and by it alone. And now the territory of physiology is being scanned in many directions from the same point of view. As time presses I must close with a few mere hints of what is being done. I call your attention particularly to the fact that the activity of a salt toward an organism may depend upon three factors. Those are the two ions and the salt itself. Even the latter may be present in the organism, since the dilution is a limited one. Osmotically the ions and molecules behave alike, and the actions involving withdrawal of water must be considered in the light of this fact. Specific actions, however, are perceptible and we naturally attribute the similar behavior of different salts in this respect to the presence of the same ion in each. Thus we explain the poisonous influence of mercury salts to the mercury ion. In this direction important conclusions have already been reached.[1] For example, not all mercury compounds contain the ion in question, but in precisely these cases the poisonous property is absent. The toxic effect varies also from case to case according to the degree of ionization.

---

[1] ROSEMANN, *loc. cit*; GALEOTTI, "Ueber die Arbeit welche die Nieren leisten," *Archiv f. Anat. und Physiol.* (1902), p. 200.

---

[1] PAUL, *Hamburger Naturforscherversammlung*, 1901.

LECTURE VII

PHYSICAL CHEMISTRY AND PHYSIOLOGY

Enzymes, Their Preparation and Nature—Enzymes as Catalytic Agents—Chemical Equilibrium—Graphic Representation of Incomplete Chemical Interactions—Incomplete Actions Occur When Heat Change is Small—Application to the Behavior of Enzymes—Illustrations—The Synthesis of Amygdalin.

THIS second lecture on physical chemistry in its relation to physiology will be devoted to the consideration of the behavior of enzymes. As we all know, this name has been given to certain exceedingly complicated compounds which are found in animal and vegetable organisms. They have the property of producing chemical changes without being themselves altered in the process, and they bring about such changes in quantities of other bodies which are altogether out of proportion to their own amount. One of the oldest examples is furnished by the substance emulsin, which is contained in almonds. Wöhler found that it had the power to decompose amygdalin, which is found along with it, and is otherwise a stable body. The products of this decomposition are glucose, benzaldehyde, and hydrocyanic acid.

An example from more recent work may be placed alongside of this. As we know, sugar, or rather a special kind of sugar known as glucose, is decomposed by yeast into alcohol and carbon dioxide. This is in fact the alcoholic fermentation which is used in the preparation of spirituous liquors. Until a few years ago this transformation was considered to be one of the life processes of yeast. This is one of the lower organisms and seemed to develop in the course of fermentation by consumption of sugar and production of carbon dioxide and alcohol. Recently, however, Buchner has shown that this influence of yeast can take place without the presence of the living organism. If the yeast is killed by warming to a definite temperature, a substance may be extracted from it which can still produce fermentation, although it possesses neither life nor organized form. This substance is called zymase, and when its solution is mixed with glucose the effervescence resulting from the evolution of carbon dioxide and the accompanying production of alcohol occur in the normal manner.

The known enzymes are now very numerous, and, what is more important, it appears as if all fermentations were produced by bodies of this class. This is important on account of the physiological significance of the fact that what was formerly supposed to be due primarily to the necessary presence of a living organism is now found to be produced by unorganized substances. It still remains true, however, that animals and plants are concerned in the formation of these substances. The moment, however, that these actions of enzymes were found to occur without the direct intervention of life, the changes became classifiable as catalytic actions. These changes must indeed be regarded as complicated, when we consider the nature of the enzyme and its mode of action. They are widely separated in this respect from the actions of platinum sponge, by the help of which, for example, water is produced from its elements. In spite of this, however, physical chemistry is in a position to make some suggestions, since some of the conclusions to which it points may be applied irrespective of the mechanism of the change involved. The effective range of these suggestions is not at all diminished by complexity in the nature of the action. In treating the subject from this point of view, therefore, the composition and chemical character of enzymes do not require to be considered in detail. They seem to be most nearly allied to the albumins. We may hope that an exact study of their internal structure will some day be able to explain their remarkable specific actions It will explain, for example, precisely why one enzyme acts upon glucose, while another acts upon amygdalin. For the present, however, we approach the subject from an entirely different point, and regard the enzymes simply as bodies which produce or hasten chemical reactions without ultimately themselves suffering any change. It may be that they do undergo changes of a transitory kind, and that, to give a simple illustration, the enzyme combines with the original body and then gives off decomposition products in such a way that it is ultimately regenerated. Still, consideration of these details, as we have said, is not essential, and provided the enzyme is ultimately recovered unaltered, the principles of which we are about to speak are applicable.

These principles depend upon chemical equilibrium. We have already mentioned this subject several times. I recall to your mind the fact that some chemical reactions, including the best-known ones, such as the formation of water from its elements, proceed to completion. In the case cited, for example, the explosive gas undergoes complete transformation. Nevertheless, this sort of change is by no means general, but quite the contrary. I take, for example, the action of an acid, such as acetic acid, upon ethyl alcohol. This proceeds slowly at the ordinary temperature, and more rapidly when heat is applied, and yields finally ethyl acetate and water.

$$C_2H_4O_2 + C_2H_6O = C_2H_3O_2 \,.\, C_2H_5 + H_2O$$

The essential point, however, as was shown by Berthelot and Péan de St. Gilles, is that this change does not proceed to complete consumption of the constituents. On the contrary, the change ceases when two-thirds of the material has been transformed. Thus, if we take 60 g. of acetic acid and 46 g. of alcohol, only 59 g. of ethyl acetate are formed, instead of the theoretical amount (88 g.). As we all know, the explanation lies in the fact that water and ethyl acetate act upon one another to produce the reverse change. A similarly limited action also takes place when we start with 88 g. of ethyl acetate and 18 g. of water. The condition of seeming rest which is finally reached is the result, therefore, of two opposite reactions which were proceeding with equal speed, and are represented by the expression:

$$C_2H_4O_2 + C_2H_6O \leftrightarrows C_2H_3O_2 \;\; C_2H_5 + H_2O \,.$$

This presents the final condition and gives also the relative proportions of the materials.

It may perhaps be well to put this concretely in still another form. Let us imagine that the change in composition from left to right is represented in Fig. 6 in such a way that A is the mixture of acid and alcohol, and B that of ester and water. Then, at the point C, two-thirds of the distance from A, is shown the final condition of both systems when equilibrium is reached. Let now the chemical change be represented by a rolling ball, which proceeds along the line DEF and comes to rest at the lowest point E. The formation of ester now corresponds to the motion along DE, the reverse action, the saponification, to that along FE. In order to enable the figure more closely to represent the facts, we must suppose further that the ball has no inertia, and that therefore it does not reach the point E with its maximum velocity and proceed beyond it, but that it gradually moves more and more slowly until it comes to rest at this point.

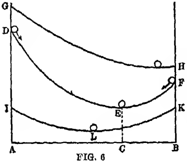


FIG. 6

In this diagram we may place also the reactions which appear to be complete, for it has gradually come to be seen that even in their case a limit is reached. Only this limit lies, as we might represent it by the curve GH, so far to one side that the most delicate means of investigation are required to show that the change has been in reality partial at all. Our conceptions have in fact fundamentally changed in respect to these matters. Formerly cases of chemical equilibrium appeared to be exceptional. Now we have every reason to think that, at least where homogeneous mixtures of the systems under transformation are in question, as is the case in solutions, the attainment of equilibrium is invariable, and complete change is to be considered as only apparent.

We may now proceed a step farther, however. We can perceive a means of predicting which actions will proceed in such a way that the existence of a limit will not be perceptible at ordinary temperatures, and will become noticeable only when, at higher temperatures, the limit has been displaced toward the middle. Such reactions must be those which are accompanied by a great development of heat. In this we encounter once more the principle of maximum work (p. 31) in a somewhat changed form. To this class belong, for example, those changes which are accompanied by combustion or explosion.

The state of affairs is quite different when the development of heat is small, and the existence of a large group of cases in which the heat development is actually zero at all temperatures is very striking. These reactions are somewhat out of the ordinary line. They are those in which optically active substances, which have the power of rotating the plane of polarized light, are turned into bodies of exactly the same composition with precisely the opposite optical action. Thus ordinary (dextro-) tartaric acid may be changed into lævo-tartaric acid, a substance having the same composition, whose structure, however, is a mirror-image of that of the former. Here the heat developed by the change is absolutely zero, as we should expect from the identity of the internal dimensions of both molecules. In correspondence with this, the position of equilibrium lies exactly half way between the two kinds, and leans therefore neither to the side of the dextro- nor to that of the lævo-acid. It produces an inactive mixture of the two in precisely equal proportions. This state of affairs may thus be represented (Fig. 6) by the symmetrical curve IK, with the ball at the lowest position L.

Let us now return to the action of enzymes and note the prominent fact that the chemical changes which they bring about are invariably such as are accompanied by small developments of heat. Thus, the modification which butter undergoes when it becomes rancid is a reaction whose heat change is almost zero. From this it follows almost of necessity that an easily observable state of equilibrium must be reached, although the question might be asked whether, since a strange agent like an enzyme is concerned, complete change would not after all occur. To this question our diagram (Fig. 6) gives a decisive answer. Such a displacement of the equilibrium would correspond to the movement of the ball upward from the lowest position, and would represent therefore an accomplishment of work. This, however, is excluded if the enzyme acts as a catalyzer, and is found unchanged at the end. Even if we assume a slight change or weakening of the enzyme, the reply is not materially affected, since this would bring about nothing more than a slight accomplishment of work, and therefore a slight displacement of the equilibrium.

Having reached this point, we are now forced to accept a surprising conclusion in regard to the influence of enzymes. If these are not in a position to displace the equilibrium point, and this equilibrium point is noticeably divergent from the condition of completed action, it follows of necessity that when a certain change can be produced or hastened the opposite change must be influenced in precisely the same way. Some confirmations of this conclusion are already known. Thus Lemoine found that the formation of hydrogen iodide from hydrogen and iodine is hastened by platinum sponge, and that this foreign body is not affected by the change. This being the case, the limit of the change, which is reached long before complete union has occurred, is not affected by the platinum. The expectation that platinum would hasten the decomposition of hydrogen iodide, which follows necessarily from these facts, was confirmed by experiment. Again, quite recently, Brereton Baker has found that perfectly dry ammonium chloride is volatile without decomposition and that perfectly dry hydrogen chloride does not combine with ammonia to form ammonium chloride. A trace of moisture, however, which instantly leads to the formation of ammonium chloride from its constituents in the cold, assists the opposite reaction in precisely the same way and produces decomposition at a high temperature.

In the case of enzymes the situation is certainly less simple, since, with the complex organic compounds which are concerned, so many different kinds of reaction are possible. Thus instead of the reverse action a quite different one might occur. If this possibility were excluded we might state as a generalization that the enzymes must have the capacity to build up from their parts those bodies which they have the power to decompose into the same constituents. If this were true, a very simple means would be furnished for the synthesis of physiological substances of the very highest interest. Thus, since the albumins under the influence of ferments like trypsin are decomposed into simpler compounds, we should see a prospect of reconstructing them, with the help of trypsin, from the same products of decomposition.

Let us now turn to what has actually been done in this direction. The first realization of what has been hinted at above seemed to have been achieved by Hill, when, as a result of his work on reversible hydrolysis,[1] he found that maltose, which contains twelve carbon atoms in the molecule and can be split by an enzyme contained in yeast, with formation of glucose:

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6 \ ,$$

could be reconstructed from glucose by the help of the same enzyme. Unfortunately it was discovered later that the form of sugar produced by this reversal is not maltose, but, at all events for the most part, the isomeric isomaltose.[2] The synthetic powers of the enzymes have not been discredited by this, however, for the very latest discovery of Emmerling[3] has come to the rescue. He has shown that amygdalin, which is decomposed by emulsin into glucose, benzaldehyde, and hydrocyanic acid,

$$C_{20}H_{27}NO_{11} + 2H_2O = 2C_6H_{12}O_6 + C_7H_6O + HNC \ ,$$

[1] *Jour. Chem. Soc.*, Vol. LXXIII (1898), p. 634; *Ber. d. deutsch. chem. Gesell.*, Vol. XXXIV, p. 1380.

[2] EMMERLING, *Ber. d. deutsch. chem Gesell.*, Vol. XXXIV, pp. 600, 2206.

[3] *Ibid.*, p. 3810.

can be reconstructed from the glucoside of mandelic nitrile and glucose by means of the yeast maltase, which Hill had also employed:

$$C_{14}H_{17}NO_6 + C_6H_{12}O_6 = C_{20}H_{27}NO_{11} + H_2O\,.$$

Although obviously in this direction only a few preliminary steps have yet been taken, it cannot be doubted that these discoveries will lead to an exceedingly rich field of work. They may possibly conduct synthetic organic chemistry to the solution of the highest problems. It is to be hoped that they will do so, not only because unsuspected possibilities for the construction of those substances which play so important a part in living organisms is offered, but also because the methods which are involved approach much more nearly the natural modes in which the substances in question are formed than do our ordinary syntheses. Indeed, these methods may actually be the natural ones.

PHYSICAL CHEMISTRY AND GEOLOGY

LECTURE VIII

PHYSICAL CHEMISTRY AND GEOLOGY

The Formation and Structure of Geological Salt Deposits—Early Study of Deposition from Solutions Containing Several Salts, by Usiglio—The Proportion of the Constituents as Well as Their Solubility to be Considered—The Modern Method of Study and Graphic Representation—The Case of a Single Salt and Water at a Fixed Temperature, 25°—The Case of Two Salts Simultaneously Present at 25°—The Case of Three Salts at 25°—The Problem of Sea-Water at 25°, with All Salts Present.

I SHALL devote the last two lectures to the relation of chemistry to geology, and in doing so shall bring together the results of investigations which I have made during the last few years, for the most part in association with Meyerhoffer.[1]

We may say in a general way that in the formation of the crust of the earth two processes falling within the territory of physical chemistry have played an important part:

1. The cooling and gradual solidification of masses originally fluid.

2. The drying up of originally liquid solutions, accompanied similarly by the gradual formation of solid deposits.

In both cases displacements of conditions of equilibrium are concerned. These are partly of a physical nature, such as gradual solidification and crystallization, and partly consist in displacements of chemical equilibria under the influence of changes in concentration and temperature.

---

[1] *Sitzungsber. der königl. preuss. Akad. der Wissensch.*, von 1897 an.

By way of reaching speedily the subject which is to concern us, it must be stated that the great processes of evaporation which are of geological importance have taken place in sea-water, or at least in a salt solution having a composition closely approaching that of the sea. This process is primarily responsible for the formation of the great salt deposits which now constitute the most important commercial source of common salt. If rock salt or sodium chloride were alone concerned, and sea-water contained no other substances, the problem of evaporation would hardly require any explanation. The water would leave and the salt would remain behind. The fact of chief importance technically, as well as mineralogically and geologically, is that the subordinate constituents of sea-water have to be considered. These are such substances as magnesium, potassium, and calcium in the form of chlorides and sulphates, as well as boric acid, carbonic acid, bromine, iron, and so forth. During the process of evaporation these substances accumulated for the most part in the mother-liquor until, as at Stassfurt, they ultimately formed a mineral layer on the top of the rock salt. They were originally set aside as valueless, and were classed by the miners as stripping. Now they have acquired a technical importance which far exceeds that of the rock salt lying below them, and the mode of formation of some thirty minerals, some in, some over, and some under the common salt, presents a problem whose solution could not be approached until very recently. We have in fact only lately come into possession of adequate means of attacking the problem and of thoroughly comprehending the law describing the deposition of materials from complex solutions.

By way of giving some insight into the situation, it should be mentioned that the stratified deposits, as we study them from the bottom upwards, may be divided into four main regions. The first two are named in order after two compounds of calcium which are contained in them. They are the anhydrite ($CaSO_4$) and the polyhalite ($2CaSO_4 . MgSO_4 . K_2SO_4 . 2H_2O$) regions. In both of these rock salt alternates regularly with thin layers, in the first of anhydrite and in the second of polyhalite. These are commonly regarded as marking years, and their formation is supposed to be connected with the seasons. The two upper regions are named after prominent magnesium compounds which are contained in them, namely, kieserite ($MgSO_4 . H_2O$) and carnallite ($MgKCl_3 . 6H_2O$). Rock salt is a uniform companion of these substances, although it is present in constantly diminishing proportions. This rather regular system of deposits is usually regarded as the product of direct evaporation of a salt solution similar to sea-water, and is therefore designated as primary. Certain other products are secondary and have been formed from the above by subsequent change, and especially by the action of water. Thus sylvite (KCl) was formed from carnallite, and kainite ($MgSO_4 . KCl . 3H_2O$) from the latter and kieserite.

This conception of the relations of the substances was first subjected to experimental investigation by the Italian chemist Usiglio.[1] He evaporated sea-water on a large scale and obtained as deposits calcium carbonate, sodium chloride, gypsum ($CaSO_4 . 2H_2O$), magnesium sulphate with seven and with six molecules of water of crystallization, schönite ($MgSO_4 . K_2SO_4 . 6H_2O$), potassium chloride, carnallite, and magnesium chloride. Some very important constituents of the mineral deposits, and especially anhydrite, polyhalite and kieserite, which lend their names to three of the four regions, were lacking. We shall presently learn why experiments like those of Usiglio fail to correspond completely with the natural processes. It was necessary, therefore, to take up the problem by a different method and in a more general manner, and to secure an answer to the question, What is the influence, not only of the composition of the solution, but also of temperature, pressure, and time on the nature of the deposits which are formed? We have only recently been able successfully to attack this question and to answer it.

---

[1] *Ann. de Chim. et de Phys.* (3), Vol. XXVII (1849), pp. 92, 172.

I must first give prominence to the fact that one frequently stated and indeed seemingly obvious principle is nevertheless not strictly correct. This principle is to the effect that the order in which deposits appear must correspond to the order of solubility in such a manner that the most soluble substance must come out last. It is certainly true that taken as a whole the order of the natural deposits is in harmony with this, and that first a slightly soluble calcium salt appears in the form of anhydrite, then its combinations with more soluble sulphates, as polyhalite, then the easily soluble magnesium sulphate by itself as kieserite, and finally the very soluble carnallite. Yet it would obviously be quite possible to produce a solution so rich in magnesium sulphate and so poor in gypsum that when it was concentrated the more soluble magnesium sulphate would appear first. Thus the composition of the solution plays an important part in the order of the deposits. Then, too, while the solubility is also a determining factor, we have to remember that it may vary very widely under the influence of other bodies which are simultaneously present.

Let us first consider these two factors, the composition of the solution and the solubility of the substances present of it, and let us restrict the influence of temperature, pressure, and time by choosing a definite point, 25°, for the first, atmospheric pressure for the second, and crystallization in the manner common in laboratories for the third. In this way we approach most closely the conditions of Usiglio's experiments, while considering the problem involved in the gradual removal of the solvent as a general one. The concentration of sea-water will thus arise as a special case, when in the course of this more general study the constituents of sea-water receive special consideration.

Among the constituents, of course, the amount of sodium chloride occupies the place of chief importance. After it come the chlorides and sulphates of magnesium and potassium. Thirdly, there are the calcium salts, and with these, for our present purpose, the list closes. Now, in order to give a clear view of the composition of sea-water, let us express the proportion of the constituents, which, strange to say, if we exclude the calcium salts, is the same all over the earth, in molecules:

$$100NaCl + 2\ 2KCl + 7.8MgCl_2 + 3.8MgSO_4 .$$

Let us now develop the laws pertaining to the crystallization, step by step, taking the dissolved substances into account one by one.

If a single salt is present the situation is very simple. As evaporation takes place the saturation point is finally reached and the salt in question separates out until the whole has dried up. So soon, however, as two salts are present, the question arises, Which will crystallize first, and when will the second appear? Let us answer this question, taking as the two salts potassium chloride and sodium chloride at 25°. We have only to remember that if, for example, the solution contains so much potassium chloride that this salt is the first to separate in the solid form, further concentration must gradually increase the content of sodium chloride until this substance also begins to appear. From this moment onward the solution retains its composition unchanged. It simply diminishes in volume and deposits both salts until the solvent is all gone. Obviously the same ultimate solution must be obtained if we start from the opposite side with a sufficient excess of chloride of sodium. The whole situation is thus clear when we know the composition of the final solution which is saturated with both salts. Analysis of a solution which has been agitated for a sufficient length of time with an excess of both salts at 25° gives the following result:

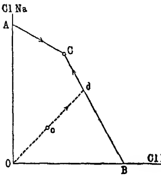


FIG. 7

$[100H_2O + 89NaCl + 39KCl]$ (C, Fig. 7).

Thus, solutions which contain a greater ratio of sodium chloride to potassium chloride than $89 \times 58.5 : 39 \times 74.5$ will first deposit sodium chloride. In the opposite case potassium chloride will first appear.

Here, then, the relations are still of a simple character. In order that they may retain their comprehensibility when applied to more complicated cases, let us represent them graphically as in Fig. 7. To complete the figure, we require the solubility of sodium chloride, which is expressed by the formulæ

$[1000H_2O + 111NaCl]$ (A, Fig. 7),

and that of potassium chloride, which is

$[1000H_2O + 88KCl]$ (B, Fig. 7).

Now, with O as origin, let us lay off the amount of sodium chloride in the vertical direction and that of potassium chloride horizontally to the right. When this is done the data given above lead to three points, which we have designated in order C, A, B, and if we now connect A and B with C the line AC represents saturation with sodium chloride, while the proportion of potassium chloride increases. Similarly, the line BC stands for saturation with potassium chloride, while the content of sodium chloride increases.

It is now easy to see what must take place when any solution is concentrated. Let it be an unsaturated one, corresponding in composition to a point c inside the area OACB, its situation being given by the proportions of the respective chlorides. When evaporation begins, the relative proportions of the chlorides do not alter, but their quantity, calculated on the basis of the number of molecules in every $1000H_2O$, must increase. This change corresponds to a motion away from O along a straight line connecting O with c, that is to say, a motion along cd. When BC is encountered at d, this means that separation of potassium chloride begins, and here a change in the direction of the motion occurs which reflects an ensuing phenomenon. The direction taken is now towards C, or, in other words, is away from B in the direction of the arrow. When C is reached, simultaneous separation of both salts begins, and this stage reaches its conclusion when the solution has dried up. This must ultimately occur to every solution after this point has been reached, and we therefore name C the *final point of crystallization.*

We may now read in this graphic representation the law upon which ultimately, even in the most complicated cases, the progress of crystallization is founded. In words, it amounts to this, that in depositing its contents the solution gradually varies its composition *away from* that of a solution which is saturated with the substance being deposited at the moment and contains nothing but this substance. The principle becomes quite clear if we reverse the process which takes place during crystallization from an evaporating solution, *i. e.*, if we add continually water and the salt which is being deposited. Under these circumstances obviously the solution tends to become more and more a saturated solution of this salt alone, since the other constituents, whatever they may be, must gradually become relatively negligible in quantity.

In the graphic representation given in Fig. 7 we may perceive four applications of this law. If potassium chloride separates on BC we move in the direction away from B, where saturation with potassium chloride is represented; if sodium chloride appears upon AB we move away from A, where saturation with sodium chloride exists. If both salts are deposited at C, we remain at rest at C, since we can move neither towards A nor towards B, and everything else is excluded. If nothing separates at c, we proceed in the direction away from O, where the solution contains nothing whatever. All this, which in the present case is obvious, will later furnish us with valuable guidance. Let us proceed then to the consideration of a more complicated case.

Keeping the salts found in sea-water in view and looking at the composition of sea-water,

$$[100NaCl + 2.2KCl + 7.8MgCl_2 + 3.8MgSO_4] ,$$

we could now add to the combination sodium chloride and potassium chloride, a third salt, *e. g.*, magnesium chloride. We shall reach the goal more quickly, however, if we first consider the salts potassium chloride, magnesium chloride, and magnesium sulphate, and only at the very end take into consideration the chloride of sodium, which is always present in excess.

Proceeding systematically we have first the combination potassium chloride and magnesium chloride, that is to say, a combination with a common acid, then that of magnesium chloride and magnesium sulphate with a common base. Further, however, if the problem is stated in a general form, potassium sulphate, which has not been mentioned, must be taken into account, since it may arise out of potassium chloride and magnesium sulphate. The third combination is thus magnesium sulphate and potassium sulphate with a common acid, and the last will be potassium sulphate and potassium chloride with a common base.

Let us now collect into one table the data in regard to solubility which are required as the basis of graphic representation for this cycle of substances. Three of them have just been given. For the present purpose, however, we now represent all the salts in equivalent amounts, so that potassium chloride is in double molecules.

SATURATION WITH	IN MOLS. PER 1000 MOLS. H_2O			
	K_2Cl_2	$MgCl_2$	$MgSO_4$	K_2SO_4
A. Potassium chloride	44	. .	.	.
E. Potassium chloride and carnallite . . .	5½	72½	....	..
F. Magnesium chloride and carnallite	1	105	. .	. .
B. Magnesium chloride		108	.	....
G. Magnesium chloride and $MgSO_4 . 6H_2O$.	...	104	14	..
H. $MgSO_4 . 7H_2O$ and $MgSO_4 . 6H_2O$.	.	73	15	..
C. $MgSO_4 . 7H_2O$......	...		55	. .
J. $MgSO_4 . 7H_2O$ and schönite........	....	....	58½	5½
K. Potassium sulphate and schönite.	. .	.	22	16
D. Potassium sulphate.	.. .	.	...	12
L. Potassium sulphate and potassium chloride	42	..	...	1½

The presentation of the whole of this material graphically makes the understanding of it much easier. The rectangular axes in the plane of the paper can be retained and from their point of intersection at O (Fig. 8) the four single salts, potassium chloride, magnesium chloride, magnesium sulphate, and potassium sulphate, can be laid off in the

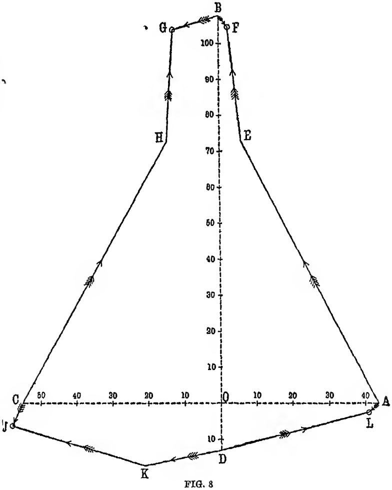

B
G
F
100
90
80
H
E
70
60
50
40
30
20
10
C
50
40
30
20
10
0
10
20
30
40
A
J
L
10
D
K

FIG. 8

directions, A, B, C, and D, respectively. The four combinations which they form, two by two, fall then within the quadrants lying between the axes. We obtain in this way a fashion of representing the facts something like Fig. 7

repeated four times. In this case, however, in three of the quadrants a complication arises from the existence of an intermediate compound. Between A, saturation with potassium chloride, and D, saturation with potassium sulphate, there is only the point L, where the solution is saturated with both. Between A and B, however, carnallite ($KCl . MgCl_2 . 6H_2O$) appears, and thus two determinations are necessary, which have been added at E and F and stand for saturation with carnallite and potassium chloride in the one case, and the same compound with magnesium chloride in the other. In the same fashion between B and C magnesium sulphate with six molecules of water crystallization appears in GH and between C and D the mineral schonite ($K_2Mg(SO_4)_2 + 6H_2O$) along JK. The progress of crystallization, using the same principle as before, is just as easy to follow, and is indicated by the arrows which in each quadrant are directed towards a so-called final point of crystallization. In this diagram these points are F, G, J, and L.

So far, however, we have only considered a part of the possibilities, for solutions are entirely lacking which contain everything, that is to say, chlorine and sulphuric acid, potassium and magnesium. The experimental treatment of this question may best be shown by means of an example. Let us start from L (Fig. 8), where the solution at 25° is saturated with potassium chloride and potassium sulphate simultaneously. Taking care that both potassium salts are present in excess and in contact with the solution, we add magnesium in the form of chloride or sulphate. The solution then takes up magnesium, but remains still saturated with potassium sulphate and potassium chloride. Finally its capacity for taking up magnesium becomes exhausted, and a solid magnesium salt is deposited. This in the case before us is schönite ($K_2Mg(SO_4)_2 . 6H_2O$). After this, further addition of the magnesium salt will not lead to any being dissolved; the consequence will simply be an increase in the amount of schönite. The solution will retain its constant composition, since it is and remains saturated with potassium sulphate and potassium chloride. We determine the composition of this solution by analysis, using a mixture which at 25° after prolonged agitation is seen to be in contact with all the three salts and is found to have attained a constant composition. The result is represented by the following formula:

$$[1000H_2O + 25K_2Cl_2 + 11MgSO_4 + 21MgCl_2] .$$

Our task is thus finally limited to finding the solutions saturated with three salts and analyzing those solutions. Many such are *a priori* possible, if we consider the seven different compounds which have to be taken into account. The possible number would be:

$$\frac{7 \times 6 \times 5}{1 \times 2 \times 3} = 35 .$$

As a matter of fact, however, only a few of these possibilities are realized, and when a solution obtained in the above manner is systematically evaporated at 25°, and the salt deposits are continually removed, the possibilities which are actually realized are found to be limited to four, in addition to the one described.

After potassium chloride and schönite have come out, magnesium sulphate with seven molecules of water of crystallization appears as an additional salt. The deposit having been removed, this hydrate of magnesium sulphate and potassium chloride are now deposited until finally magnesium sulphate with six molecules of water of crystallization is added to these two salts as a new constituent. From this point onward the hexahydrate of magnesium sulphate with potassium chloride crystallizes until carnallite makes its appearance. After this the hexahydrate of magnesium sulphate with carnallite constitute the deposit until magnesium chloride appears, and now the solution dries up completely to a mixture of the three last-named substances.

Collecting once more the quantitative measurements connected with these deposits, we have the following table:

SATURATION WITH	IN MOLS. PER 1,000 MOLS. H_2O		
	K_2Cl_2	$MgCl_2$	$MgSO_4$
M. Potassium chloride, potassium sulphate, schönite	25	21	11
N. Potassium chloride, $MgSO_4$ $7H_2O$, schönite	9	55	16
P. Potassium chloride, $MgSO_4.7H_2O$, $MgSO_4$ $6H_2O$	8	62	15
Q. Potassium chloride, carnallite, $MgSO_4$ $6H_2O$	4½	70	13½
R. Magnesium chloride, carnallite, $MgSO_4$ $6H_2O$	2	99	12

The next thing is to represent these numbers graphically, and when this has been done we are presented with a complete view of the whole process of crystallization.

To do this a third dimension is obviously required. We add a third axis passing through O, vertical to the former system of axes (Fig. 8), and along this we lay off the number of molecules. In practice this may be done conveniently by means of a model consisting of a piece of wood in which vertical needles are set at the proper places, with their lengths adjusted to the number of molecules. A horizontal projection on this model is shown in Fig. 9, whose border obviously coincides with the outline of Fig. 8, and whose points M, N, P, Q, and R represent the above data.[1] This having been done, each pair of points representing saturation with the same two salts—for example, M and L, where in both cases saturation with the sulphate and chloride of potassium exists—is connected by a line.

These lines divide the figure into areas, each of which corresponds to saturation with a definite salt, as follows:

EQPNMLA	Potassium chloride
EQRF	Carnallite
FRGB	Magnesium chloride
RGHPQ	$MgSO_4 . 6H_2O$
PHCJN	$MgSO_4 . 7H_2O$
JKMN	Schönite
KMLD	Potassium sulphate

The progress of crystallization is given in each area by lines which proceed away from the points which represent saturation with the body itself, as a single constituent. Thus, in the potassium chloride area, these lines proceed from A in all directions.

---

[1] It may be remarked that this method of presenting the facts is not influenced by the condition in which one supposes the salts to be present in the solution; that is to say, whether they are K_2Cl_2 and $MgSO_4$ or $MgCl_2$ and K_2SO_4.

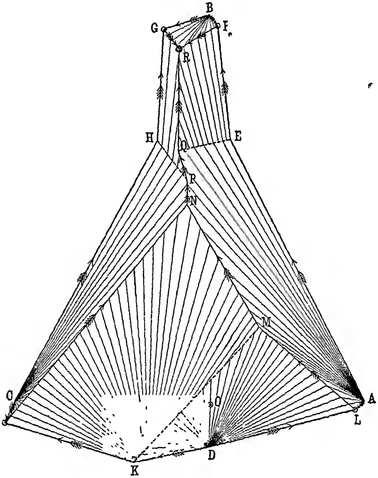


FIG. 9

Let us apply this now to a particular case, taking, for example, a solution containing a gram-molecule of magnesium chloride and a gram-molecule of potassium sulphate. The preliminary evaporation without any deposit appearing corresponds to motion from the origin in the vertical direction until the area lying immediately above it—that is to say, the potassium sulphate area—is encountered. Potassium sulphate should separate out, and this, as a matter of fact, is just what occurs. We next expect a movement away from D until the limit KM is reached, where schönite should appear, and this expectation is also fulfilled in practice. If the salts as they come out are always removed, the deposition of schönite corresponding to a movement across the schönite area in the direction of the lines drawn upon it takes place until MN is reached, indicating the beginning of potassium chloride crystallization. This salt does actually appear next. Here the course of the paths of crystallization from both sides shows that with further concentration we remain[1] on the line MN until at N magnesium sulphate begins to be deposited. The rest of the changes may be read from the diagram in the same manner. Not only can we thus follow the progress of the crystallization, qualitatively, however. We can calculate the quantity of each substance which will be separated when a given point corresponding to a known composition is reached. The results agree exactly with experiments which have been made in a variety of ways. Thus Fig. 9 contains the basis for understanding and even predicting the whole process of crystallization.

When a beginning has been made in applying the principles according to which crystallization proceeds, the additional compounds occurring in the natural deposits can easily be introduced into the scheme. These are sodium chloride and the salts of calcium.

---

[1] For this reason boundaries like MN are named *bases* of crystallization. There are four of these proceeding from the final points of crystallization, L, J, G, and F. All meet together at the common final point R.

We shall not attempt to carry out this extension in detail. It may simply be mentioned that a scheme corresponding to Fig. 9 can be, and has been, laid out for the case in which all the solutions are saturated with sodium chloride at 25°, a state which corresponds with natural conditions. So far as the salts of calcium are concerned, their solubility is so small that they do not seriously alter the composition of the solutions themselves. It is only necessary to determine from which of the solutions calcium in the form of gypsum ($CaSO_4 . 2H_2O$), anhydrite ($CaSO_4$), syngenite ($CaSO_4\ K_2SO_4 . H_2O$), or some other form, will be deposited.

LECTURE IX

PHYSICAL CHEMISTRY AND GEOLOGY

The Influence of Time and of Variations in Temperature and Pressure on Deposition—The Time Factor and Delayed Crystallization—Several Compounds, Found in Nature, Do Not Appear at All in Laboratory Experiments on Deposition, but Can Be Included in the Scheme by the New Method of Agitation with Solutions—The Behavior at Temperatures above 25°—New Minerals Formed above 25° and Absent at 25°—New Combinations of Minerals Possible above 25°—Disappearance above 25° of Minerals Formed at that Temperature—The Influence of Possible Changes in Pressure Too Slight to Affect the Results.

THAT to which in this second lecture on geology I should like chiefly to devote my attention is the consideration of the parts which time, temperature, and pressure play in modifying the nature or amount of the deposits. Their importance diminishes in the order stated.

Time is the most important factor, and yet its influence is the most difficult of the three to determine by laboratory experiments. In direct experiments on the crystallization of sea-water, such as were made by Usiglio, obviously time received less consideration than anything else, and a better approach to a knowledge of the geological processes is hardly possible by his method, in consequence of the speed of the experiments. The method of treating the subject described here is more favorable in this respect. At first it is true the results accord essentially with those of Usiglio. In the course of further investigation, however, one compound after another is obtained which, on account of retardation of quite unexpected extent, is entirely missed when the ordinary method of crystallization is employed. Such retardations are known to you in the case of so-called supersaturated solutions, such as that of Glauber's salt. Supersaturations of this kind, however, are easy to avoid by introduction of the substance, here Glauber's salt, in respect to which supersaturation exists. In imitation of this we have always prepared our saturated solutions by long agitation with the salts in respect to which saturation is required. After this has been done, a filtered sample is brought in contact with well-developed crystals of the same salts, in order that the question of the existence of saturation may be definitely settled. This procedure had seemed to make success only a question of hours, or at most of days, until we unexpectedly found that some compounds whose formation in the solutions under investigation was possible at 25°, nevertheless totally failed to put in an appearance. These, not to mention the salts of calcium, were leonite, $K_2Mg(SO_4)_2 . 4H_2O$; kainite, $MgSO_4 . KCl . 3H_2O$; and kieserite, $MgSO_4 . H_2O$. Even exceedingly slow crystallization with the addition of the compounds themselves did not remove the condition of supersaturation in the case of these bodies.

Precisely in this region the new method of treatment shows its superiority, since it is not dependent upon direct crystallizations. It relies on the determination of solubility data, and relatively few of these, to give a complete view of the whole plan of crystallization, both qualitatively and quantitatively. Now, data of this kind, in the case of the bodies just mentioned, may be obtained in spite of the tendency to retardation, although agitation may sometimes have to be continued for weeks.

Let us now present the data obtained from such experiments:

SATURATION WITH SODIUM CHLORIDE AND	MOLS. WITH 1000 MOLS. H_2O				
	Na_2Cl_2	K_2Cl_2	$MgCl_2$	$MgSO_4$	Na_2SO_4
O.	55½	....	. ..	...	....
A. $MgCl_2 . 6H_2O$	2½	....	103	...	....
B. KCl	44½	19½	..	. ..	.. .
C. Na_2SO_4	51	....	.	.	12½
D. $MgCl_2 . 6H_2O$, carnallite	1	½	103½	....	...
E. KCl, carnallite	2	5½	70½	.	....
F. KCl, glaserite	44	20	..	. .	4½
G. Na_2SO_4, glaserite	44½	10½	. .	..	14½
H. Na_2SO_4, astrakanite	46	....	.	16½	3
I. $MgSO_4 . 7H_2O$, astrakanite	26	...	7	34	.. .
J. $MgSO_4 . 7H_2O$, $MgSO_4 . 6H_2O$	4	....	67½	12	....
K. $MgSO_4 . 6H_2O$, kieserite	2½	....	79	9½	....
L. Kieserite, $MgCl_2 . 6H_2O$	1	...	102	5	....
M. KCl, glaserite, schönite	23	14	21½	14	....
N. KCl, schönite, leonite	14	11	37	14½	....
P. KCl, leonite, kainite	9	9½	47	14½	....
Q. KCl, kainite, carnallite	2½	6	68	5	....
R. Carnallite, kainite, kieserite	½	1	85½	8	....
S. Na_2SO_4, glaserite, astrakanite	42	8	..	16	6
T. Glaserite, astrakanite, schönite	27½	10½	16½	18½	....
U. Leonite, astrakanite, schönite	22	10½	23	19	...
V. Leonite, astrakanite, $MgSO_4 . 7H_2O$	10½	7½	42	19	. .
W. Leonite, kainite, $MgSO_4 . 7H_2O$	9	7½	45	19½	....
X. $MgSO_4 . 6H_2O$, kainite, $MgSO_4 . 7H_2O$	3½	4	65½	13	...
Y. $MgSO_4 . 6H_2O$, kainite, kieserite	1½	2	77	10	.. .
Z. Carnallite, $MgCl_2 . 6H_2O$, kieserite	0	½	100	5	....

Those data may be represented by a model, in the way previously described. A projection of this model is shown in Fig. 10. The basal plane is in so far different that the sodium chloride is not represented in the model, while the sodium sulphate is not taken into account in the number of molecules, in consequence of the relation

$$Na_2SO_4 = Na_2Cl_2 + MgSO_4 - MgCl_2$$

The latter is measured off upon an axis OC, which bisects the angle DOB. The areas correspond to the following substances:

Area	Formula	Mineralogical Name
1. ALZD	$MgCl_2 . 6H_2O$	Bischofite
2. BFMNPQE	KCl	Sylvite
3 CGSH	Na_2SO_4	Thenardite
4. DZRQE	$KMgCl_3 . 6H_2O$	Carnallite
5. FMTSG	$K_3Na(SO_4)_2$	Glaserite
6 SHIVUT	$Na_2Mg(SO_4)_2\ 4H_2O$	Astrakanite
7. JXWVI	$MgSO_4 . 7H_2O$	Reichardtite
8 JXYK	$MgSO_4 . 6H_2O$	(Not found)
9 KYRZL	$MgSO_4 . H_2O$	Kieserite
10. TUNM	$K_2Mg(SO_4)_2,\ 6H_2O$	Schönite
11. NUVWP	$K_2Mg(SO_4)_2, . 4H_2O$	Leonite
12. PWXYRQ.	$MgSO_4 . KCl . 3H_2O$	Kainite

and the progress of crystallization may be developed on the same principle as before.

The next thing to be considered is the influence of temperature. Solubility is, as we all know, very generally influenced by change of temperature, and such a change will therefore alter a diagram constructed for 25°. For our purpose it is important to determine what geological information

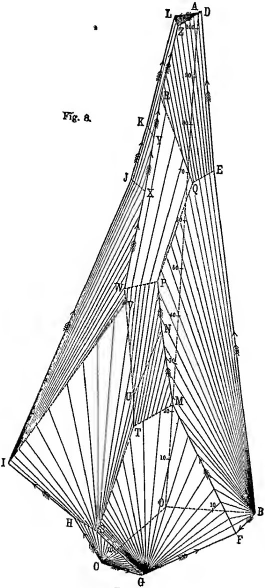


Fig. 8.
L
A
D
Z
100
90
R
80
K
Y
J
70
E
X
Q
60
50
W
P
V
40
N
30
U
M
20
T
10
I
O
10
B
H
S
10
F
O
G

FIG. 10

may be obtained in this direction. The most significant thing is the appearance of additional minerals which cannot be formed as low as 25°. Then follows the appearance of additional combinations of minerals. Finally the disappearance of some minerals is to be noted.

Among the appearances of minerals at temperatures above 25° two may be mentioned by way of illustration. Among the chlorides and sulphates of potassium, magnesium, and sodium, two known materials are absent at 25°, namely langbeinite, $K_2Mg_2(SO_4)_3$, and loeweite, $Na_2Mg(SO_4)_2 \cdot 2H_2O$. The failure of these substances to appear is not a consequence of retardation, for in the solutions in which at 25° they would first be formed, they are actually decomposed by interaction with water. Thus langbeinite becomes a mixture of magnesium sulphate and leonite according to the equation:

$$K_2Mg_2(SO_4)_3 + 11H_2O = MgSO_4 \cdot 7H_2O + K_2Mg(SO_4)_2 \cdot 4H_2O$$

and loeweite gives astrakanite:

$$Na_2Mg(SO_4)_2 \cdot 2H_2O + 2H_2O = Na_2Mg(SO_4)_2 \cdot 4H_2O\ .$$

This fact furnishes us with a hint in the determination of the temperature at which these bodies would be formed. The products of their hydration have only to be heated in contact with that solution which is saturated with them, and possesses the greatest water-withdrawing power. In the case of langbeinite this is the solution W (Fig. 10), where the necessary saturation with magnesium sulphate and leonite exists, and where, besides, kainite, with which the solution is simultaneously saturated, contributes to the water-removing power. In contact with this, langbeinite is formed from its products of hydration above 37°, while below this temperature the change is reversed. The occurrence of langbeinite in the natural salt deposits thus indicates the existence of a temperature above 37°. A similar temperature limit of 43° is found for loeweite.

Let us now turn to the second influence of temperature, that, namely, on the simultaneous occurrence of minerals. This is shown in Fig. 10 for the temperature 25°. We shall present the same figure in a simplified form, preserving all the lines of contact, but changing shapes of the areas to rectangles. We then see that glaserite, for example, can occur along with astrakanite, but not along with bischofite. This figure (Fig. 11) contains material for a great number of geological inferences.

When I was exhibiting Fig. 11 in a lecture on this subject in Strassfurt, Dr. Schwab directed my attention to "hartsalz," a mixture of kieserite and potassium chloride, which is excluded at 25°, since the two areas are separated by kainite. This problem was taken up by Meyerhoffer, who found that "hartsalz" is a product peculiar to a much higher temperature, somewhere in the neighborhood of 70°. This temperature is probably the highest of which we have any indication in connection with this subject.

The third point, the disappearance of some minerals, might also be employed as a geological thermometer. Thus, the existence of reichardtite, $MgSO_4 . 7H_2O$, is determined by an upper limit of 47°, that of schönite by the temperature $47\frac{1}{2}$°.

Finally the pressure must be considered. It has often been hinted at as a possible agency in the formation of minerals, which, like anhydrite, fail to appear in laboratory

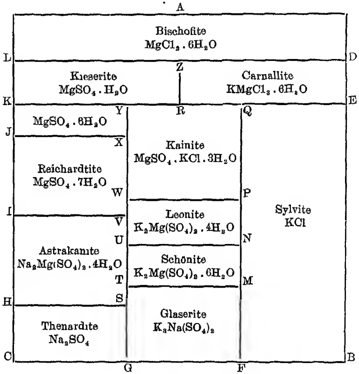

A
Bischofite
$MgCl_2 . 6H_2O$
L
D
Z
Kieserite
$MgSO_4 . H_2O$
Carnallite
$KMgCl_3 . 6H_2O$
K
E
Y
R
Q
$MgSO_4 . 6H_2O$
J
X
Kainite
$MgSO_4 . KCl . 3H_2O$
Reichardtite
$MgSO_4 . 7H_2O$
W
P
I
Sylvite
KCl
Leonite
$K_2Mg(SO_4)_2 . 4H_2O$
V
U
N
Astrakanite
$Na_2Mg(SO_4)_2 . 4H_2O$
Schönite
$K_2Mg(SO_4)_2 . 6H_2O$
T
M
H
S
Glaserite
$K_3Na(SO_4)_2$
Thenardite
Na_2SO_4
C
B
G
F

FIG. 11

experiments, when the cause of this was simply retardation. On reflection we find that the influence of pressure in the formation of natural salts must be relatively small. In the case of the Strassfurt deposits, for instance, we cannot count upon a greater depth of sea-water than 1500 meters.

Assuming the specific weight, when the deposition of salts begins, to be 1.2, this would indicate a pressure of

$$\frac{1500 \times 1.2}{10} = 180 \text{ atmospheres}$$

Now, the chief effect of the pressure is that temperatures of formation, such as the 37° in the case of langbeinite, are displaced. They are raised when, as is commonly the case with actions involving the separation of water, a simultaneous expansion takes place.

The extent of these displacements is, however, of the same order as that which the melting-points show under the influence of the same agency. It may be determined theoretically. We have measured it experimentally also in connection with the formation of the mineral tachhydrite, $Ca(MgCl_3)_2 . 12H_2O$, with the anticipated result. It was found that a single atmosphere of pressure only affected the temperature, here 22°, by a few thousandths of a degree. The actual measurement was 0.017°, which for 180 atmospheres would correspond to 3°.

Since in the case of the formation of salt deposits, according to the latest direct observations with the salt mother-liquors of Siebenbürgen by Kaleczinsky,[1] changes in temperature of 50° have to be reckoned with, the consideration of pressure is very much less important in the study of this problem than is that of temperature.

---

[1] *Über die ungarischen warmen und heissen Kochsalzseen*, Budapest, 1901.

INDEX

ACETIC ACID, 87.

ALCOHOL, 87.

AMYGDALIN, 84, 92.

ANHYDRITE, 99, 100,

ARRHENIUS, 24, 39.

ASTRAKANITE, 118.

AVOGADRO'S LAW, 17; applied to solutions, 19, 73.

BAKER, 91.

BAKHUIS-ROOZEBOOM, 25, 67.

BECKMANN, 81.

BENZALDEHYDE, 84, 92.

BERTHELOT, 17, 31, 33, 87.

BISCHOFITE, 118.

CALCIUM CARBONATE, 100.

CARNALLITE, 99, 100; graphic representation of its region of stability, 29; illustrating the new and comprehensive method of studying a problem, 25, method of manufacturing potassium chloride from, 48; three methods of splitting up, 50, transition point at −21°, 27, 34; transition point at 168°, 28.

CARNOT-CLAUSIUS PRINCIPLE, 20.

CAST IRON, white and gray, 67.

CATALYTIC ACTION, 85.

CEMENTITE, 61.

COHEN, 53, 75.

CONSERVATION OF ENERGY, 20

CRYSTALLIZATION: final point of, 104; graphic representation of, 102, 107, 112, 119, 122.

DANIELL CELL, 36.

DEPOSITION: influence of pressure on, 122, influence of temperature on, 118; influence of time on, 115.

DE VRIES, 74.

DILATOMETER; use of, in determining transition point of tin, 55.

DONDERS, 77.

DUHEM, 6

ELECTRICAL METHOD: of determining transition points, 56; of measuring affinity, 36.

ELECTROLYTIC DISSOCIATION, 39.

EMMERLING, 92.

EMULSIN, 84, 92.

ENZYMES, 84, 90.

EQUILIBRIUM, CHEMICAL, 37, 86.

EYCKMAN, 81.

FERTILIZATION, ARTIFICIAL, 80.

FERRITE, 61.

FORMULÆ, STRUCTURAL, 4.

GLASERITE, 118.

GLUCOSE, 84, 86, 92.

GOLDSCHMIDT, 47.

GRAPHITE, 61, 66.

GYPSUM, 100.

HAMBURGER, 77.

HARTSALZ, 121.

HILL, 92.

HYDROCYANIC ACID. 84, 92.

IONIZATION. and physiology, 82; theory of, 38.

IRON: transition point at 850°, 62.

KAINITE, 99.

KALECZINSKY, 123.

KEKULÉ, 4.

KIESERITE. 99, 100.

KOEPPE, 79.

KOHLRAUSCH, 41.

LADENBURG, 8, 6.

LANGBEINITE, 120, 121.

LEMOINE, 91

LEONITE, 118.

LOEB, 10, 74, 80.

LOEWEITE, 120, 121.

MAGNESIUM CHLORIDE, 100, 105.

MAGNESIUM SULPHATE, 100, 105.

MALTASE, 93.

MALTOSE, 92.

MARTENSITE, 61.

MASSART, 78.

MAXIMUM WORK: principle of, 31, 32, 35.

MEYERHOFFER, 25, 97, 121.

NERNST, 24, 41.

OPTICALLY ACTIVE SUBSTANCES, 89.

OSTWALD, 23, 41.

OSMOTIC PRESSURE, 7, 74, 76, in bacteria, 79, in blood corpuscles, 77, in plants, 76, in the eye, 78; measurement of, 81.

PÉAN DE ST. GILLES, 87.

PEARLITE, 61, 64.

PFEFFER, 7.

PHOSPHONIUM CHLORIDE, 33.

PHYSICAL CHEMISTRY: industrial applications of, 48; introduces new conceptions, 17; is not merely the use of physical instruments, 16; its founders, 23; its place in the science, 6; its three modes of application in inorganic chemistry, 24; what it has accomplished, 6; why applied chiefly in inorganic chemistry, 24.

PHYSIOLOGICAL CHEMISTRY, 9, 41.

PLAN OF THE LECTURES, 15.

POLYHALITE, 99, 100.

POTASSIUM CHLORIDE, 99, 100, 102, 105; three methods of obtaining it from carnallite, 48, 50.

POTASSIUM SULPHATE, 105.

PREDICTION OF REACTIONS, 31, 33.

RAOULT, 40, 81.

REICHARDTITE, 118

REVERSIBLE CYCLES, 21.

REVERSIBLE CHEMICAL ACTIONS, 87.

SALT DEPOSITS· stratification of, 99.

SALTS deposition of three, 106; deposition of two, 102.

SCHAUM, 53.

SCHÖNITE, 100, 109.

SCHWAB, 121.

SEA WATER, 98, 101.

SODIUM CHLORIDE, 98, 100, 102.

SOLUTIONS, SOLID, 59.

STEEL, 58; explanation of hardness of, 66; graphic representation of behavior of, 63; methods of examining structure of, 61; tempering of, 61.

STEREOCHEMISTRY, 5.

SYLVITE, 99, 100, 102, 105.

SYNGENITE, 114.

TACHYDRITE, 123.

TARTARIC ACID, 89.

TEMPERING OF STEEL, 61.

THALLIUM SULPHOCYANATE, 87

THENARDITE, 118.

THERMODYNAMICS, 20.

THOMSON, 17, 31.

TIN DISEASE, 52.

TIN: gray, 52; specific weights of white and gray, 53; transition point of, 54.

TRANSITION TEMPERATURES, in alchemic change, 25.

TRYPSIN, 92.

USIGLIO, 99.

VON JÜPTNER, 58, 62.

WINKLER, 6.

WORK: possibility of accomplishing, as measure of chemical affinity, 33, 38.

YEAST, 84, 92.

ZYMASE, 85.